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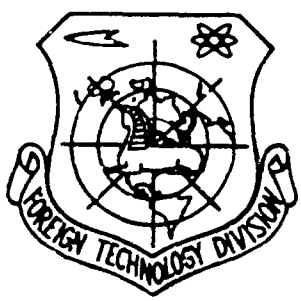
NITRIDES

by

G. V. Samsonov



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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

FOLLOWING ARE THE CORRESPONDING RUSSIAN AND ENGLISH

DESIGNATIONS OF THE TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	$\sin^{-1}$
arc cos	$\cos^{-1}$
arc tg	$\tan^{-1}$
arc ctg	$\cot^{-1}$
arc sec	$\sec^{-1}$
arc cosec	$\csc^{-1}$
arc sh	$\sinh^{-1}$
arc ch	$\cosh^{-1}$
arc th	$\tanh^{-1}$
arc cth	$\coth^{-1}$
arc sch	sech^{-1}
arc csch	csch^{-1}
rot	curl
lg	log

NITRIDES

Grigoriy Valentinovich Samsonov

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PREFACE

The principal bases of technical progress are the development of power engineering [energetics], the automation of production and the development of new materials. Such new materials must satisfy the complex requirements of contemporary technology, possessing either individual, specific, rather clearly expressed properties, or complexes of properties.

Especially great importance is being acquired by the development of materials, which can be exploited at extreme – very high, or very low – magnitudes of temperatures, pressures, velocities, stresses, radiation fluxes, gas flows.

Among such materials the most promising are the refractory metals, their alloys, and also compounds of refractory metals with nonmetals – boron, carbon, nitrogen, silicon, and so forth, many of which are already being successfully used in electronics, atomic power engineering, semiconductor and dielectric technology, space technology, contemporary machine building, metallurgy, the chemical industry, electrical technology and other fields.

Special interest is being manifested in compounds of metals and nonmetals and nitrogen, the so-called nitrides, among which many possess high refractoriness, dielectric and semiconductor properties, the ability to develop superconductivity at relatively

high temperatures, with high chemical stability in different aggressive media, wear resistance, and others — catalytical activity, low melting points, low values of hardness, lubricating properties.

The investigation of nitrides began in the first third of the past century with the works mainly of French and German naturalists, but was especially expanded at the beginning of the Twentieth Century in connection with the overall development of chemistry and the requirements of metallurgy and other fields of technology.

A considerable contribution to the investigation of the methods of production, the properties and the fields of application of nitrides was made by Russian scientists, of whom it is necessary to mention first I. I. Zhukov, who carried out a number of fundamentally important and in many respects basic works on nitrides in the first quarter of the Twentieth Century.

Important works in this direction were made abroad by G. Brauer, R. Junza, G. Hägg, N. Schönberg, E. Gebhardt, C. Agte, E. Griederich, L. Sittig. In the USSR works on the synthesis and investigation of nitrides of the transition metals and certain nonmetals were carried out in the Physicochemical Institute im. L. Ya. Karpov under the leadership of B. F. Ormont, on electron diffraction investigation of nitrides — in the Institute of Crystallography of the Academy of Sciences of the USSR under the leadership of Z. G. Pinsker. In recent years works have expanded on refractory nitride materials (D. N. Poluboyarinov, N. I. Voronin, S. G. Tresvyatskiy), comprehensive investigations were conducted in the Institute of Problems of the Science of Materials of the Academy of Sciences of the Ukrainian SSR.

However the problem of investigating and applying nitrides is still far from being solved — all the preceding investigations have only outlined the most promising directions for subsequent, more thorough works.

The information on nitrides is extremely scattered in various original works, which appeared during the last one and a half centuries which hampers their application and the creation of a single concept about this important class of inorganic compounds.

In the present book the author has set as his purpose to fill in this gap to some degree and to assist in the subsequent investigation and expansion in the application of these compounds in practice, and to familiarize the large community of metallurgists and chemists with them.

It is natural, that this first attempt cannot be free from deficiencies.

The author considers it his duty to note the contribution in the investigation of nitrides, which was made by his talented pupil, T. S. Verkhoglyadova, who prematurely departed this life, and also to express his deep gratitude to P. V. Gel'd for the great labor in reviewing this book and the valuable remarks, which made it possible to substantially improve the book, and also to all the Soviet and foreign scientists, who furnished impressions in their works, which substantially facilitated the writting of this book.

INTRODUCTION

Among the compounds, formed by the elements of the periodic system with nonmetals, the compounds with nitrogen – the nitrides – occupy a special place with respect to the atom ability of the nitrogen to accept electrons from a partner with the completion of the stable (in an energy regard) configuration of s^2p^6 electrons or to give up an electron to a partner with the formation of the stable sp^3 configuration. In the first case the compounds formed possess a clearly expressed ionic bond, in the second – a typical metallic bond, and in both cases they are accompanied by a larger or smaller fraction of a covalent bond, which becomes predominant or practically the only one in compounds of nitrogen with nonmetals. Thus, a large part of the nitrides is characterized by resonance [hetrobonding or mesomersism] binding with broad ranges of a fraction of different types of this binding, to which the variation in the nature and the values of the physical and chemical properties correspond. Thus, if nitrides of nonmetals are chiefly covalent compounds of the dielectric class, then the nitrides of the transition metals with a deficet of nitrogen as opposed to stoichiometric amount and certain nitrides of saturated composition (CrN and others) possess semiconductor properties with a mixed ionic-covalent-metallic-type of bonding, and nitrides of the alkali and alkaline-earth metals are ionic-covalent compounds. At the same time a large part of the nitrides of the transition metals of saturated composition with respect to nitrogen are typical metallic substances.

The relative simplicity of the electronic rearrangements of the nitrogen atom itself and the electronic structure of nitrides makes them convenient "model" objects for studying chemical binding. The variety of nitride phases with broad limits of variation in the nature of the binding and the physicochemical properties ensures the application of nitrides in different regions of technology and reveals broad potential possibilities for creating nitride phases and materials based on them with the previously mentioned properties.

The mechanism of nitride formation is of great interest, especially in the case of the effect of nitrogen on simple substances. With respect to the concepts developed in the present monograph, of a nitrogen molecule has a structure of the type $sp^3:sp^3$, where the stable sp^3-configurations are bonded to each other by paired electrons. This ensures the high bonding strength and a certain chemical inertness of molecular nitrogen, and also the latter recombination of atomic nitrogen into molecular nitrogen. Therefore, for the formation of nitrides it is necessary either to disturb a covalent bond which requires sufficiently strong excitations of a thermal or electrical nature, or it is necessary to have a high acceptor capacity of the atoms of the nitrided substance, or, finally, the transfer by the nitridated substance of electrons to the nitrogen with the formation of s^2p^6-configurations and the disturbance as a result of this of the structural configuration of molecular nitrogen of the type: stable configuration – covalent bond – stable configuration. Thus, the study of the process of the nitridation of simple substances makes it possible to draw important conclusions concerning the nature of chemical binding in nitrides and those energy changes, which occur with the destruction of the nitrogen molecule and the formation of nitride phases.

With the formation of nitrides from complex compound of the ionic type (by their thermal dissociation) nitrides of the ionic type will also be frequently formed; this type is not inherent to the stable state and is metastable. This pertains to nitrides of

transition metals, which when obtained by the usual methods in the stable state have compositions, not characteristic for ionic compounds, and with the thermal dissociation of certain compounds compositions are obtained, characteristic for ionic substances.

The peculiarities of the electronic structure of nitrides determine their remarkable properties – the high superconductivity of certain of them, the high values of thermo-emf, the great magnitudes of the width of the forbidden zone, the extraordinarily low or extraordinarily high values of hardness and so forth, which by itself evokes the necessity of a detailed study of the nature of these compounds. However, in spite of the accumulated material about the properties, the structure and the peculiarities of the processes of producing nitrides, there are as yet essentially no works, which would make it possible to examine all data from a single point of view, in particular from the point of view of the electronic structure of nitrides. Although the concepts available at the present time concerning this question chiefly bear a qualitative character, nevertheless the application of the indicated concepts can lend much to the understanding of the nature of nitrides.

In this monograph the author has set himself the task not only collecting as much as possible of the available information on nitrides, but also of drawing attention to the interesting or hard-to-explain peculiarities of the nitride phases and the processes of their formation.

CHAPTER I

THE STRUCTURE AND PROPERTIES OF NITRIDES

1. The Electronic and Crystalline Structures of Nitrides

The problem of the electronic structure of nitrides is part of the great problem of the electronic structure of compounds of metals and nonmetals, on the one hand, with nonmetals, on the other, and at the present time certain steps in its solution are being made mainly as part of the investigation of compounds of transition metals with nonmetals. This, naturally, is connected in the most intimate manner with the development of concepts about the electronic structure of the transition metals.

Characteristic for the nitrides of transition metals is the formation by them of interstitial phases, i.e., phases with simple structures, structured according to the type of the introduction of nonmetal atoms into the crystal structure of a metal. The condition of the formation of such phases is the satisfaction of the Hägg rule, according to which the radii ratio of a metal atom R_{Me} and an atom of nonmetal R_X should satisfy the criterion

$$R_X : R_{Me} < 0{,}59.$$

As follows from the data of Table 1, for nitrides of the transition metals the ratio $R_X:R_{Me}$ is always smaller than Hägg's critical value.

Table 1. Ratio $R_N:R_{Me}$ for nitrides of transition metals.

Metal	$R_N:R_{Me}$	Metal	$R_N:R_{Me}$	Metal	$R_N:R_{Me}$	Metal	$R_N:R_{Me}$
Sc	0,43	Y	0,39	La—Lu	0,37—0,40	—	—
Ti	0,48	Zr	0,44	Hf	0,44	Th	0,39
V	0,52	Nb	0,48	Ta	0,48	—	—
Cr	0,51	Mo	0,50	W	0,50	U	0,46
Mn	0,53	Tc	0,51	Re	0,51	—	—
Fe	0,56	Ru	0,52	Os	0,52	—	—
Co	0,56	Rh	0,52	Ir	0,51	—	—
Ni	0,56	Pd	0,51	Pt	0,51	—	—

The basis of interstitial structure of a metal lattice, into the tetrahedral or octahedral pores of which of nonmetal atoms are introduced; with which a certain distortion of the lattice can occur. The interstitial phases with the composition Me_4X will usually form CFC- [cubic, face-centered] lattice (C12), with the composition Me_2X – a hexagonal compact one (H12) with the composition MeX-CFS ,C12), or CBS [cubic, body-centered] (C8), or a simple hexagonal one (H8) [777]. Since the number of octahedral pores in H12 and C12 lattices is equal to the number of metallic atoms, and the number of tetrahedral pores is twice as large, then with the placement of nonmetal atoms in octahedral pores with saturated composition it is MeX, and with the occupation of the tetrahedral pores with saturated composition it is MeX_2.

The introduction of nonmetal atoms into the lattices of transition metal atoms is not a simple placement of nonmetal atoms in the pores of a metal lattice with the formation of compounds of the inclusion complex type [clathrate compounds] [778]; but is accompanied by the formation of strong chemical bonds between the metal and nonmetal atoms, fundamentally changing their chemical identity and physical properties.

A great number of works have been dedicated to the clarification of the nature of such chemical bonds, especially during the past 20-25 years. One of the first attempts to understand the nature and peculiarities of chemical binding in interstitial phases was

undertaken by A. Kh. Breger [779]. He demonstrated that in bringing about chemical binding there participate both d-, s-valence electrons of a transition metal, and also s-, p-valence electrons of nonmetals, which will form resonance bonds in six directions (in the case of octahedral coordination) practically uniformly, since all six neighbors in the lattice of the NaCl type are located at identical distances from the central atom. Consequently, with respect to these concepts, it is necessary to give preference to the so-called atomic bonds, i.e., mainly covalent bonds, characterized by a distribution of electronic density, similar to the distribution in diamond (electronic density between the closest atoms has finite value, not differing by an order of magnitude from the maxima of the electronic density of corresponding atoms). In this work it is demonstrated that the covalent bond is affected by a considerable fraction of the ionic bond, increasing with the transition from C to N and O, and also (in isoelectronic structures) – from V to Ti. Below it will be shown that this point of view, little known earlier, is finding at the present time numerous confirmations.

Great renown has been obtained by the point of view of the nature of chemical binding in interstitial phases, developed by Ya. S. Umanskiy [777, 781] and consisting in the fact that with the introduction of nonmetals into the lattices, formed by metal atoms, "metallizing" of the nonmetal atom occurs, i.e., the transfer to it of all or a definite part of the valence electrons in a certain electronic association, common for metal and nonmetal atoms, and mainly determining the metallic nature of the bond between the atoms. It is assumed that the valence electrons of the nonmetals partially pass over to the unfilled electronic d-subgroup of transition-metal atoms which leads to an increase in the binding energy in the crystal lattice, bringing them closer in their properties to elements with more build-up shells and higher binding energies, like W and Mo. Since the ionization potential of nitrogen is greater than carbon, the electrons of nitrogen atoms, apparently, participate little in the build up of the d-shell of the metal, and the bonding force with

the formation of nitrides hardly increases [78]. Although at the present time these concepts have been completely rejected in practice, they were the initial stage in the development of the theory of interstitial phases.

The author of this work has made an attempt to impart a certain quantitative appraisal of the possibility and the degree of transition of valence electrons of nonmetal atoms on the d-states of transition-metal atoms [782], assuming, after Ya. S. Umanskiy that the probability of such a transition in general should increase with the reduction of the ionization potential of the nonmetal atom. The probability of the transition of the valence electrons of atoms of a given nonmetal for the d-state of the metal is increased, obviously, with the reduction of the principal quantum number of valence d-electrons (i.e., proportionally 1/N, where N – the principal quantum number), thanks to the possibility of the occupation by an electron of a site on the d-shell with the greatest release of energy, and also with the reduction of the number of electrons on the d-shell of an isolated transition metal atom (proportionally 1/n, where n – the number of electrons on the d-shell), due to the tendency to fill this shell. Consequently, the probability of the filling by an electron of a nonmetal atom of vacant sites and the d-shell of a metal atom is determined by the product of particular events, i.e., by the number 1/nN.

The correlation of the physical properties of interstitial phases and the indicated criterion, called the "acceptor" capacity of a transition metal atom, is completely satisfactory and made it possible from definite positions to explain the nature of many properties of interstitial phases. To this question are dedicated our numerous works; some of which were completed jointly with V. S. Neshpor and other colleagues (see, for example, [783-790]). It is necessary to note that these correlations have not lost their significance at the present time, however in the number 1/nN a completely different significance is placed than the capacity following from the concepts of Umanskiy of transition-metal atoms to "accept" valence electrons of a "metallized" nonmetal atom.

In his work Parthe [791] indicates the necessity of three-dimensional bonds in lattices of interstitial phases and phases related to them for explaining the observed high values of the physical properties and the dense packing of structural elements of the smallest size.

According to Rundle [792], with the introduction of a nonmetal into a transition metal the Me-Me bond is weakened, and the electrons accomplishing this bond in the metal partially change to an Me-X bond. He assumes that the bond in lattices of interstitial phases are chiefly covalent (as does Breger also), and for interstitial phases, formed by transition metals of the first row, four electron pairs resonate with respect to six bonds (formed by the three 2p-orbits of the nonmetallic atoms). Such bonds are "electron-deficient", similar to the bonds in boron hydrides (boranes), and are characterized by the fact that the paired-electron structure of the bond should leave the stable bonding orbitals unused. In such a case several atomic orbitals can be combined to form a bonding orbital with a minimum of energy – such a combined orbital contains only one electron pair, but can effectively bind more than two atoms. Thus the concept of semibonds arises, which will be formed, when one element should have more stable bonding orbits than valence electrons (i.e., it should be in general a metal), and the other component should have relatively few bonding orbits and be in general a nonmetal; also the electronegativities of both components should not substantially differ. Phases of interstitial of the MeX type with the structure of NaCl conform to these three conditions, where X = C, N and sometimes O (if there is no significant difference in electronegativity; fluorine is always too electronegative and similar types of phases will not form). With the increase of the atomic number of the transition metal in the group an even greater number of electrons of the metal participates in the Me-Me bonds and a smaller number of them is transmitted to an Me-X bond which causes, in the opinion of Rundle, difficulty in the formation, for example, by the transition metals of the VI group of phases of the MeX type with the structure of NaCl.

In the work of Engel [793] concepts have been developed about the fact that each atom has fixed and a clearly definite pattern of quantum states, which is essentially invariable; in any chemical transformations, allotropic modifications transitions of electrons from one quantum state to another are observed, but without variation in the general quantum pattern which is constant for a given atom. To a certain extent Engel approaches concepts concerning sets of stable electronic configurations, about which more will be indicated below. In examining a compound of transition metals with nonmetals, Engel considers that the ionization of atoms of nonmetals with the transfer of a part of the valence electrons to the d-state of atoms of transition metals is the most energetically efficient (spd-hybridization he considers improbable because of energy considerations, since mixed compounds are usually weaker [794]). Thus, Engel's views in practically no way differ from the concepts of Umanskiy and the concepts, developed in our previous works. Kiessling occupies the same positions [795], confirming that the transfer of electrons by nonmetal atoms to metal atoms strengthens the Me-Me bond, which is determinant for interstitial phases as compared to the Me-X bond. Similar views were also developed by Robins [796], who considers, however that for the formation of interstitial phases the Me-X bond is determinant. Robins considers that the principal characteristics of interstitial phases is the relationship of the electronic concentration of the bond to the coordination number of atoms of the metal.

Toman [948] also considers that in compounds with nonmetals the 3d-transition metals decrease the fullness of the sp-band, capturing electrons from it, where this ability to capture is reduced in the direction Cr > Mn > Fe > Co. For nickel the least ability to capture electrons is practically equal to zero.

Recently concepts have been developed, based on the variation of the density function of the states near the Fermi surface with the variation of the concentration of valence electrons for the atom [797-802]. It has been shown that the extremes for the density

curve of the states correspond to certain extreme values of the electrophysical, thermodynamic and other properties. Of special interest is the work of Dempsey [802], in which although the point of view of Umanskiy is taken about the acceptor character of d-elements, and also the donor role of nonmetals, nevertheless there is indicated the substantial role of the covalent bond between atoms of the transition metals and its absence in practice between metals and nonmetal atoms. Attention is turned to the existence of specially stable zones, containing about 6 electrons (5.5-6.5 electrons) to which the extreme properties of metal with nonmetal compounds correspond.

Not having the possibility to examine in detail all the indicated concepts, it is necessary to note that in the majority of the given theories it is assumed that in the formation of compounds of the type of interstitial phases the nonmetal atoms transfer part of their valence electrons to the d-states of transition-metal atoms. The degree of transfer is reflected on the nature of the dependence of the density of the states on the number of valence electrons on the atom. The special, extreme properties of a substance correspond to the extreme values of the density of the states.

A somewhat different approach to the consideration of the electronic structure and properties of compounds of metals and nonmetals with nonmetals is possible [803]. In the formation of a solid from isolated atoms the valence electrons of the latter are partially localized near the cores of the atoms, and partially go over to a nonlocalized state. The localized fraction of the valence electrons forms a rather broad spectrum of configurations, distinguished by their energetic stability, i.e., by the reserve of free energy, so that along with very stable configurations to which the minimum of free energy corresponds, there appear fewer and very unstable ones. Assuming that the statistical weight of the stablest (in an energetic regard) electronic configurations of atoms substantially exceeds the statistical weight of the unstable ones, it is possible to ascribe to each atom states, corresponding

to a limited number of the stablest configurations, calling the latter stable. Between the stable configurations and the nonlocalized part of the valence electrons an exchange is carried out, responsible for the bond between the stable configurations, and consequently the cores of the atoms with each other. Between the nonlocalized electrons a strong negative interaction is carried out, which leads to the repulsion of the stable configurations and the cores of the atoms by each other, which cause disintegration of the crystal lattice and weakening of the bond between the atoms. These initial circumstances make it possible to examine from single point of view the peculiarity of the electronic, crystal structure and the properties of the elements and their compounds. It is expedient to subdivide all chemical elements into three basic groups by the criterion of the configuration of the valence electrons of their isolated atoms:

1) s-elements, having external s-electrons with completely filled or completely unfilled, deeper lying electronic shells;

2) ds- and fds-elements, the atoms of which have incomplete d- or f-shells;

3) sp-elements, having sp-valence electrons.

To the first group belong the nontransition metals, to the second – the transition metals, to the third – the nonmetals and so-called semimetals.

Transition metals. The maximum number of electrons on the d-shell of the transition metals is equal to 10, and on the f-shell – 14. In the formation of a metallic crystal from isolated atoms of d-transition metals the localized part of the valence electrons can, as was noted, form any configurations, among which the stablest (in an energy regard) for d-elements are d^0 (identical to an underlying s^2p^6-configuration), d^5 and d^{10}. The energetic stability of such configurations was demonstrated in the works on the ligand

field theory [804, 805]. The stabilization energy of a crystal field in the contemporary theory of catalysis is equal to zero with the number of electrons on the d-shell, equal to 0, 5, and 10 [806]. In works [807, 808] the spherical symmetry of the indicated configurations was demonstrated, to which the minimum free energy should correspond. In work [809] the stability of d^5- and d^{10}-configurations was established from the point of view of their energetic efficiency in optical terms, where the conclusion concerning the greater stability of d^5-configurations was made. The great stability of the semifilled d- and f-states was also demonstrated in work [5]. The resistant or stable configurations are the basis of the covalent bond. According to Pauling [810, 811], the maximum covalency is observed in the middle of each period of the system of elements.

The distribution of valence electrons was established by X-ray spectral investigation (with the transition of atoms from an isolated state to the state of a metallic crystal) for this ensuring a covalent bond (localized electrons) and collectivized bonds (nonlocalized electrons) (Table 2).

Table 2. Distribution of valence electrons for atoms of transition metals and the statistical weight of atoms with d^5-configurations in metallic crystals.

Metal	Number of valence electrons (d + s)	Localized electrons	Nonlocalized electrons	Literature	Static weight of atoms with d^5-configurations
Sc	3	—	—	—	18
Y	3	—	—	—	22
La	3	—	—	—	23
Ti	4	—	—	—	43
Zr	4	~2,6	~1,4	[812, 813]	52
Hf	4	—	—	—	55
V	5	—	—	—	63
Nb	5	~3,7—3,9	~1,1—1,3	[814]	76
Ta	5	—	—	—	81
Cr	6	~3,5	~2,5	[815]	73
Mo	6	~5	~0,95—1,05	*	88
W	6	—	—	—	94

*According to M. I. Korsunskiy and Ya. Ye. Genkin.

Assuming that the atoms, having in the isolated state a number of electrons on the d-shell nd $\leq$ 5, will mainly form only the stable configurations d^0 and d^5 of localized electrons, the statistical weight of d^5-configurations of atoms in metallic crystals of zirconium, niobium and chromium can be determined.

Proceeding from these results, the statistical weight of d^5-configurations for the remaining transition metals with nd $\leq$ 5 (using the number 1/Nn) can be approximately evaluated.

Similar data can be determined in determining according to the value of the Hall constant the number of current carrier in a unit cell on one atom, assuming a one-zone model (which, in turn, is justified by the localization of a part of the valence electrons near the cores of atoms of transition metals) and considering the current carriers a nonlocalized part of the valence electrons. A corresponding calculation, carried out by V. A. Gorbatyuk (Kiev Polytechnic Institute) and in work [1037] led to approximate results. Thus, the statistical weight of d^5-configurations, according to his data, was equal to: for Ti – 44%, Nb – 76%, Mo – 86%, Ta – 78%. A deviation was observed for chromium (83%), vanadium (78%), tungsten (81%) which is explained by the inaccurate determination of the Hall constant.

Thus, with an increase in the number d-electrons in the valence shell of isolated atoms there is an increase in the statistical weight of atoms, possessing d^5-configurations in metallic crystals. With an increase in the principal quantum number of valence d-electrons the energetic stability of d^5-configurations is increased.

For d-elements with $5 < n_d \leq 10$ it is possible to assume the presence of atoms with the two stablest electronic configurations d^5 and d^{10}, where the statistical weight of atoms, possessing d^{10}-configurations, increases with the increase in n_d.

The essential difference between metallic crystals with $n_d \leq 5$ and $n_d > 5$ is the fact that for $n_d \leq 5$ a considerable part of nonlocalized electrons is characteristic, whereas for metals with $n_d \geq 5$ the electrons, liberated in the formation of d^5-configurations, are practically completely used for the formation of d^{10}-configurations. This, in particular, is apparent from the values of the number of current carriers on the atom, equal to for Fe – 0.1, Co – 0.19, Ru – 0.04, Pd – 0.13, Pt – 0.5 [1037] that indicates the considerable "mobilization" of all electrons for the construction of stable configurations.

An analogous pattern is observed for f-elements, where the metallic crystals of elements with $nf \leq 7$ are combinations of atoms with f^0 and f^7-configurations and a considerable number of nonlocalized electrons, and with $nf > 7$ – combinations of f^7- and f^{14}-configurations with a small number of free electrons, where the stablest is the semifilled f^7-state, and the energetic stability of the corresponding f-states is increased with an increase in the principal quantum number of f-electrons.

In all cases an increase in statistical weight, the energetic stability of stable configurations and a corresponding decrease in the statistical weight of nonlocalized electrons causes an increase in the bonding forces, hardness, and melting points.

Nontransition metals. In the joining of s-metal atoms into crystals, apparently, for metals, having an s^1-valence electron, the joining into s^2-pairs, having spherical symmetry and accordingly high stability; in the case of s^2-metals – the disturbance of the pairs for the possibility of organizing of the compound between the atoms. The energetic stability of s^2-configurations decreases with the increase in the principal quantum number of s-valence electrons. The statistical weight of s^2-configurations sharply decreases with the possibility of the transfer of part of the s-electrons to completely vacant deep-lying d- or f-shells (for example, for potassium, silver).

For metals of the beryllium subgroup s → p-transfers are possible with the transformation of s^2-configurations into sp-configurations. Due to a decrease in the energetic stability of any sp-configurations with an increase in the principle quantum number of sp-valence electrons (see below), this s → p-transfer is especially clearly expressed for beryllium, weaker for magnesium and for calcium is practically completely suppressed by the transfer of part of the s-electrons to energetically stable d-states which subsequently develops for strontium, barium, and radium.

Nonmetals. For nonmetal atoms, having in isolated state sp-valence electrons, the tendency toward the formation of more energetically stable sp^3- and s^2p^6-configurations is characteristic. If an s^2p^6-configuration can be really called stable and efficient from the point of view of the energetic state of the atom, then the sp^3-configuration is not stable in isolated atoms; it arises due to the effect of the field of the crystal lattice [809] and can be called quasi-stable. The energetic stability of monotypic sp-configurations always decreases with an increase in the principle quantum number of the sp-valence electrons (for example, in the carbon group – the decrease in the width of the forbidden zone, the hardness, the melting point from diamond to germanium, the degeneration of sp^3-configurations for tin at normal temperatures, for lead – at any temperatures, the severe delocalization of electrons, appearance of high plasticity).

All elements, located to the left of the nitrogen group (Be, B, C, their analogs in corresponding groups), tend due to s → p-transfers and the mutual exchange of electrons to acquire the maximum statistical weight of the most energetically stable sp^3-configurations; on the other hand, the elements, located to the right of nitrogen (O, F and their analogs in the groups), tend to build up to a stable s^2p^6-configuration. Nitrogen and its analogs with respect to the group occupy an intermediate position. On the one hand, a nitrogen atom, having in an isolated state a configuration of s^2p^3-valence electrons, is transformable: $s^2p^3 \rightarrow sp^4 \rightarrow sp^3 + p$ with the formation of sp^3-configurations and the transfer to a

partner of one p-electron, and on the other – can accept electrons from a partner by combination with the formation of s^2p^6-configurations. This peculiarity of the nitrogen atom determines the electronic structure of its compounds with metals – nitrides and the compounds of nitrogen with nonmetals.

Proceeding from these concepts, certain general, and also concrete considerations about the electronic structure of nitrides and their physical and chemical properties can be expressed.

Nitrides of nontransition metals. The low ionization potentials of atoms of alkali metals mainly causes the transfer of their valence electrons to nitrogen atoms with the formation of nitrides of the Me_3N composition which are compounds of the ionic type. Along with this the transfer by nitrogen atoms of the highly mobile p-electron to atoms of alkali metals with the formation MeN_3 azides is possible, where, for example, for sodium, potassium and so forth, the formation of an azide is even more probable than of a nitride, in spite of the ionization potential decreasing in this direction. This is explained by the fact that beginning with potassium the filling of the deep-lying d-states occurs, the stability of which increases with the increase in the principle quantum number, which causes the transfer of the highly mobile electron from the nitrogen atom to an atom of an alkaline metal.

In the formation of azides (MeN_3) the determining factor is the grouping of the nitrogen atoms, therefore the frequencies of the oscillations of a linear N_3-group in different azides differ from each other insignificantly [824].

Analogous phases are formed by the metals of the copper subgroup, the atoms of which can chiefly transmit valence electrons to nitrogen atoms with the formation of a combination of d^{10}- and s^2p^6-stable states with a less expressed nature of ionic bond as compared to nitrides of alkali metals (since for the latter two s^2p^6-configurations

are combined, and for nitrides of copper and others d^{10}- and s^2p^6-configurations, i.e., configurations, typical for metallic and ionic bonds). This, in particular, causes the semiconductor (and not the dielectric) properties of metal nitrides of the copper subgroup, and also the appearance of the cubic structure (and not the tetragonal or hexagonal).

The composition of the nitrides of beryllium, magnesium and the alkaline earth metals corresponds to the formula Me_3N_2, which indicates the transfer of valence electrons of the metal to the nitrogen atoms with the formation of s^2-combinations (for Be) or s^2p^6-configurations (for all others) with s^2p^6-configurations of the nitrogen atoms. Due to the appearance for calcium of the possibility of the transfer of part of the valence electrons to vacant d-states the nitrogen complex with the transfer of part of the electrons of nitrogen atoms to calcium is complicated which causes the formation of the pernitride Ca_3N_4. The increase of the energetic stability of the d-states causes for strontium the appearance of still a greater number of nitride phases, including the subnitride Sr_2N, possessing a metallic nature (an analogous subnitride phase also exists for barium).

In metal nitrides of the zinc subgroup, as well as in metal nitrides of the copper subgroup there will be formed combinations of the two stable d^{10}- and s^2p^6-configurations (Me_3N_2) with the cubic lattice corresponding to these combinations.

Nitrides of transition metals. With the formation of nitrides of transition metals there is assumed the formation for nitrogen atoms of both s^2p^6- and also sp^3-configurations, the relationship of the statistical weights of which depends on the peculiarities of the partner in the compound. In proportion to the increase of the statistical weight of d^5-configurations of atoms of a transition metal in a metallic crystal the possibility of the transfer of nonlocalized electrons to nitrogen atoms should decrease with the

formation by the latter of s^2p^6-configurations, i.e., the statistical weight of the d^5- and s^2p^3-configurations increases and the statistical weight of the d^5- and s^2p^6-configurations of the atoms of metal and nitrogen, entering into the composition of the nitride decreases.

In that same direction those properties of the nitride phases should increase, the increase of which is connected with the increase of the statistical weight of the most energetically resistant stable configurations and the decrease of the statistical weight of the nonlocalized electrons, but up to a definite limit, since in the case of the very high statistical weight of the d^5-configurations of the metal atoms, the atoms of nitrogen cannot acquire s^2p^6-configurations and their highly mobile electrons (higher than the sp^3-configuration) cause intense disintegration of the lattice.

Substantial results in the study of the nature of chemical bonding in nitrides, especially of the transition metals, were obtained with X-ray spectral investigations [227, 228, 836-841, 971]. In [228] there is indicated the displacement of the relative maximum electronic density in titanium nitride toward the nitrogen atom and the appearance of a strong fraction of ionic bonding [840] in contrast to titanium carbide, where the equal affiliation of the electronic aggregate is assumed to metal and to nonmetal. Analogous conclusions are drawn in [227]. With the replacement of nitrogen atoms in titanium nitride by carbon atoms (starting with a 30% concentration of carbon in C + N) the pattern of the chemical bonds sharply changes, which substantially departs from additivity [837]. The X-ray spectral investigation of vanadium nitride in comparison with vanadium oxide V_2O_5 makes it possible to discuss the greater fraction of covalent bonds in the nitride [836].

On the basis of X-ray spectral study of chromium nitrides, carried out in work [815], the conclusion was drawn about the transfer of part of the valence electrons of chromium to nitrogen

in the process of forming nitrides, and also about the greater Me-Me interaction in Cr_2N as compared to CrN and the strong Me-N interaction in the CrN lattice.

The authors [839] indicate the exclusion of part of the valence electrons from the metal atom in niobium nitride.

Similar views were developed by Hume-Rothery [409], who considers that the introduction of nitrogen into iron leads to the acceptance of part of the iron electrons by the nitrogen atoms and the liberation of the corresponding 3d-states for bonding; because of this the GPU-structure of alloys of iron with nitrogen appears.

From the results of X-ray spectral investigations [841] the conclusion follows concerning the transfer of a part of the valence electrons in nitrides from the transition-metal atoms to the nitrogen atoms which agrees well with assumption about the localization in a part of the nitrides, especially of those metals, which have a low weight of stable d^5-states, valence electrons of these metals in s^2p^6-states of nitrogen.

This applies first of all to nitrides of transition metals which are clearly expressed donors of a nonlocalized part of the valence electrons (titanium, zirconium, hafnium and so forth). For nitrides of transition metals, manifesting fewer donor properties (possessing high weight of atoms with stable configurations), it is possible to speak about formation by nitrogen atoms of s^2p^6- and sp^3-configurations. This pertains, for example, to tantalum nitride, the X-ray spectral investigation of which revealed features similar to Ta_2O_3 (s^2p^6-configurations of nitrogen atoms) and to TaC, TaB_2 (sp^3-configurations of nitrogen atoms) [971].

Tendency of transition-metal atoms to transfer of part of their valence electrons to nitrogen atoms especially clearly appears in the production of nitrides by the careful decomposition of compounds,

where the metal atoms already had a typical ionic form, for example, of complex ammonium-chloride, ammonium-fluoride and other similar compounds. Metastable compounds also will be formed of the compositions $TiN_{1.16}$, $ZrN_{1.33}$; $TaN_{1.67}$ (see page 88).

Information about the character of chemical bonding in nitrides can be obtained from a consideration of the dynamics of thermal vibrations of a crystal lattice, as was done in [1029] in the processing of data on the low-temperature heat capacity of titanium and vanadium nitrides. It has been shown that the bonding forces between distant neighbors – atoms of a lattice – decrease with the transition from carbides to nitrides and further to oxides of titanium and vanadium. This corresponds to the smaller energies of atomization, melting points, hardness of nitrides as compared to carbides and is caused by the decrease in the role of collectivized electrons of the d-band in carrying out bonding between the atoms in the lattice. Also partially confirmed is the covalent nature of bonding in nitrides and other similar compounds.

Nitrides of nonmetals. The formation of nitrides of nonmetals and in general, compounds of nonmetals with nitrogen is usually connected with a minimization of the energy of the system as a result of the formation of stable sp-configurations (with a tendency toward the formation of the greatest statistical weight of atoms with the stablest sp^3- and s^2p^6-configurations).

Such general considerations about the electronic structure of nitrides find their actual reflection in the peculiarities of the crystal structure and the physicochemical properties of the individual nitride phases.

2. Physical Properties of Nitrides

Nitrides of nontransition metals [844]. The nitrides of s-elements are structured mainly after the type of compounds with high

fractions of ionic bonding, caused by the transfer of valence electrons by the metal atoms to the nitrogen atoms with the formation of high statistical weight of s^2p^6- or d^{10}- and s^2p^6-configurations (for lithium and beryllium – also of s^2-configurations). This determines the semiconductor properties of nitrides with a similar set of stable configurations. Thus, lithium nitride Li_3N up to 360°C practically does not conduct electrical current, but at higher temperatures, due to the thermal excitation of the stable configurations and the partial delocalization electrons, it begins to conduct current, acquiring the properties of a typical semiconductor. It is significant that the temperature curve of conductivity at 446°C changes direction which is connected with the disturbance at 350-360°C of one type of the stable configurations (probably, s^2), and at 446°C – of another (probably, s^2p^6). Unfortunately, the electrophysical properties of the nitrides of other alkali metals are unknown, but it is possible to make the assumption that the metallicity of nitrides should increase with the increase of the principle quantum number of the s^1-valence electrons both in connection with the decrease in the probability of the formation of stable s^2-configurations from s^1-electrons, and also due to the transition of part of the s-electrons to the d-states. This in particular, is observed for nitrides of the alkaline earth metals, for which beginning from strontium subnitrides appear with a metallic type of bond. Whereas the nitrides of beryllium and magnesium are typical dielectrics which is connected with the formation the most energetically stable s^2- and s^2p^6-configurations, on which a considerable fraction of the valence electrons is localized and for the disturbance of which high thermal or other excitations are required.

Metals of the copper and zinc subgroup form two types of stable configurations in nitrides: d^{10} and s^2p^6. This causes, as also for the nitrides of the alkali and alkaline earth metals energetic insulation of the atoms in the lattice, but less than for the latter ones, since the energetic stability of tne d^{10}-configurations is considerably less than the s^2p^6-configurations. Such substances are

semiconductors, but with less specific electric resistance, with smaller width of the forbidden zone. They are not like lithium nitride insulators at normal temperatures. Thus, the specific electric resistance of copper nitride at normal temperatures is a total of $6 \cdot 10^2$ Ω·cm.

The energetic insulation of atoms with stable configurations causes the low thermal stability of nitrides of s-metals: they decompose upon heating with the liberation of nitrogen. Those nitrides decompose more readily, in which the greatest number of valence electrons is localized in the most energetically resistant stable configurations. The same energetic insulation causes the relatively low chemical stability of nitrides of s-metals, which usually increases with an increase in the "metallicity" of the nitride phases.

Mainly the ionic nature of the bonding between metal and nonmetal atoms, and also the presence of a covalent bond between metal atoms or nitrogen atoms (in azides) makes it possible to consider these compounds structured according to the ionic-covalent type with a very small fraction of metallic bonding in certain of them.

Nitrides of transition metals. The physical properties of the transition-metal nitrides have been studied the most. The correlation of the values of these properties with number 1/Nn has been basically established which was noted above. Obviously, the true physical sense of this number consists not in the evaluation of the "acceptor ability," but in the index of the total statistical weight of the stable configurations of the atoms. Thus, the high value of 1/Nn for titanium signifies the low localization of the valence electrons in the stable configurations, and the low values of the number for metals of the triad of iron and platinoids – the high degree of localization of the valence electrons in stable states of any types, i.e., the low statistical weight of nonlocalized electrons.

In examining from this point of view the electrophysical properties of the nitrides of the transition metals of groups IV-VI of the periodic system (Table 3, Fig. 1) it is clear that the specific electric resistance regularly increases with the increase of the statistical weight of the stable configurations which is caused by the decrease in the concentration of the current carriers and the difficulty of excitation of the conductivity of electrons, entering into the composition of the increasingly energetic stable configurations. For the same causes the coefficient of thermo-emf decreases in the indicated direction. In work [816] an analysis of the values of certain electrophysical properties of nitrides was carried out on the basis of a consideration of the value $\delta = n_- u_-^2 - n_+ u_+^2$, where n_-, u_- and n_+, u_+ are respectively, the concentration and the mobility of the electrons and the vacancies. For metals of group IV the value of magnitude δ is very small which indicates an approximately equal contribution of electrons and vacancies in conductivity (let us note that for these metals there are approximately identical fractions of localized and nonlocalized electrons). For titanium the statistical weight of the d^5-configuration is equal to 43% and $\delta = +0.05$ which testifies to a certain prevalent of electron (n-type) conductivity, and for zirconium — 52% and $\delta = -0.09$ which testifies to a certain prevalent vacancy or hole (p-type) conductivity. With the transition to the nitrides of the metals of group IV (Ti, Zr, Hf) value δ increases and has a positive sign, i.e., the n-type conductivity is increased which is connected not only with the transfer of a part of the nonlocalized electrons of the metal to the nitrogen atom with the formation by the latter of a high statistical weight of s^2p^6-configurations, but also, probably, with a certain delocalization of electrons previously (in a metal crystal) localized in stable configurations. With the transition to metals of groups V-VI the difference δ sharply increases and has a negative sign, i.e., the hole contribution to conductivity is increased. It is necessary to compare this with the increase of the statistical weight of the stable d^5-states. The nitrides of these metals have mainly n-type conductivity (judging from the sign of the Hall coefficient and the difference δ) which indicates the small participation in current

Table 2. Physical properties of transition-metal nitrides.

Nitride	Nitrogen content		Coefficient of thermo-emf α, $\mu V/deg$	Specific electric resistance ρ, $\mu\Omega \cdot cm$	Hall coefficient $R \cdot 10^6$, cm^3/c	Thermal conductivity $\varkappa$, cal/cm·s·deg	Microhardness H_{Me}, kg/mm^2
	wt.%	at %					
$TiN_{0,98}$	22,4	49,8	−7,78±1,1	26±2	−0,67±0	0,046 ±0,003	1994±137
$ZrN_{0,98}$	13,2	49,8	−4,78±0,5	28±3	−1,3 ±0,2	0,049 ±0,002	1520±85
$HfN_{0,86}$	6,4	46,5	−2,96±0,6	33±5	−4,2 ±0,5	0,0517±0,006	1640±161
$VN_{0,338}$	8,5	25,3	−5,3 ±1,2	123±10	+0,9 ±0,1	—	1900±102
$VN_{0,74}$	16,8	42,4	—	—	—	—	1520±115
$VN_{0,93}$	20,5	48,3	−4,6 ±0,8	85±4	+0,45±0,16	0,0270±0,07	—
$NbN_{0,46}$	6,6	31,7	—	—	—	—	1720±100
$NbN_{0,5}$	7,1	33,5	−4,57±0,7	142±6	+1,9±0,4	0,0200±0,08	—
$NbN_{0,98}$	12,7	49,1	−1,65±0,1	85±2	−0,47±0,2	—	1396±26
$NbN_{1,00}$	13,1	50,0	−2,24	78±4	+0,52±0,19	0,009 ±0,002	—
$TaN_{0,45}$	3,4	31,2	−2,17±0,4	263±22	−0,46±0,1	0,0240±0,005	—
$TaN_{0,58}$	4,3	36,6	—	—	—	—	1220±120
$TaN_{1,01}$	7,3	50,3	−1,6 ±0,3	128±15	−3,6±0,9	0,0205±0,009	1060±72
$CrN_{0,47}$	11,2	32,0	—	—	—	—	1571±49
$CrN_{0,497}$	11,8	33,2	−2,3 ±0,2	79±5	−0,72±0,1	0,0519±0,004	—
$CrN_{0,926}$	20,0	48,1	−92±4	640±40	−265±25	0,0300±0,003	—
$CrN_{0,93}$	21,0	49,8	—	—	—	—	1093±93
$MoN_{0,5}$	6,8	33,5	+2,18±0,5	19,8±7	+2,83±1,2	0,0427±0,007	630±86

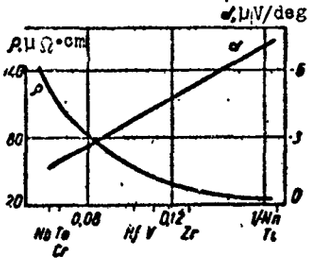

Fig. 1. The dependence of specific electric resistance and the coefficient of thermo-emf of transition-metal nitrides on the number $\xi = 1/Nn$.

transmiss..on of the stable configurations of metals and the severe delocalization of the valence electrons of nitrogen with their transition to a weakly bound state and the simultaneous formation of sp^3-configurations by the nitrogen atoms. Thus, a high statistical weight of stable d^5- and sp^3-configurations will be formed. However a high statistical weight of the nonlocalized electrons will be simultaneously which causes high fractions of the electronic part of resistance and thermal conductivity (Table 4, Fig. 2), with the exception of the nitrides of tantalum and chromium, which possess high fractions of lattice thermal conductivity [470]. This agrees well with the semiconductor nature of the nitride CrN. It is possible to compare the decrease in hardness of nitrides with the transition from group IV to metals of groups V and VI of the periodic system with the antibonding role of weakly bound nitrogen electrons [147].

Table 4. Calculated and measured electronic thermal conductivity of nitrides (cal/cm·s·deg).

Nitride	λ_p	$\lambda_{изм}$	$\lambda_p/\lambda_{изм}$	Nitride	λ_p	$\lambda_{изм}$	$\lambda_p/\lambda_{изм}$
TiN	0,062	0,046	1,34	NbN	0,026	0,009	2,97
ZrN	0,056	0,049	1,14	Ta_2N	0,006	0,024	0,25
HfN	0,047	0,051	0,93	TaN	0,008	0,020	0,40
VN	0,019	0,027	0,71	Cr_2N	0,021	0,051	0,41
Nb_2N	0,011	0,020	0,55	CrN	0,003	0,028	0,11

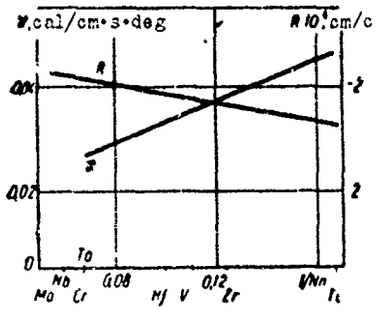

Fig. 2. The dependence of thermal conductivity and the Hall coefficient of transition-metal nitrides on the number ξ.

All nitrides of transition metals have broad regions of homogeneity. The width of the regions of homogeneity narrows from the nitrides of metals of group IV to nitrides of metals of groups V, VI, VII, and VIII which corresponds to the decrease in the statistical weight of the nonlocalized electrons of atoms of the transition metals and to the increase in the statistical weight of the stable configurations. A reduction in the regions of homogeneity is noticeable with the transition from metal nitrides with a 40-60% statistical weight of stable configurations to the large statistical weights: especially narrow are the regions of homogeneity for the nitrides of metals of group VIII, where as was mentioned above the metals the greatest total weight of d^5- and d^{10}-configurations and the small weight of nonlocalized electrons is characteristic for the metals (Table 5, Fig. 3).

Table 5. Regions of homogeneity of certain nitride phases of transition metals.

Nitride	Region of homogeneity		Nitride	Region of homogeneity	
	at. %	wt. %		at. %	wt. %
Ti_4N	Very narrow		Ta_2N	28,5—31	3,0 — 3,4
TiN	37,5—50	14,9 —22,6	TaN	44,5—47,3	5,8 — 6,5
ZrN	46—50	11,5 —13,3	Cr_2N	32 —33,3	11,3 —11,8
V_2N	25—33	8,4 —11,9	Mo_2N	32 —33	6,4 — 6,7
VN	41—50	16,0 —21,6	Mn_4N	18 —20	5,8 — 6,1
Nb_2N	28,5—33,5	5,7 —7,1	Mn_3N_2	28,3—34,7	9,14—11,9
$NbN_{0,75}$	42,9—44,0	10,2 —10,6	Mn_6N_5	38,2—41,0	13,1 —15,1
$NbN_{0,98}$	46,8—49,5	11,55—12,85	Re_2N	30 —33,3	10—11,2
NbN	50,0—50,6	13,1 —13,3	Co_2N	26 —26,7	7,7 —8

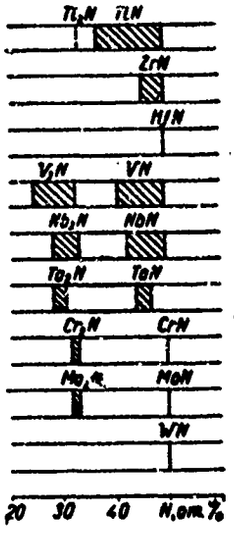

Fig. 3. The regions of homogeneity of transition-metal nitrides.

A decrease in the width of the regions of homogeneity was also noticeable with a relative reduction in the nitrogen content in nitride phases of one and the same metal which can be explained by the more severe localization of valence electrons on the Me-Me bond.

The physical properties of the nitride phases within the limits the regions of homogeneity vary rather substantially, in particular (Table 6) the specific electric resistance, the Hall coefficient, the thermo-emf [145, 202, 818], and the microhardness varv [145, 147]. As is evident from Fig. 4, the concentration dependence of microhardness of titanium nitride in the region of homogeneity has a linear character and is analogous to the dependence of the microhardness of the carbides TiC [819], ZrC, [820, 821], Ta_2C and TaC [148] on the carbon content in the regions of homogeneity. However for the indicated carbides extrapolation of the line of microhardness for a carbon content, equal to zero, gives roughly the values of the microhardness of the corresponding metals, whereas this is not observed for titanium nitride. Consequently, in crystal lattices of nitrides (in contrast to carbides) the character of the electronic structure, the chemical binding, the distribution of electronic density differs substantially from those in metals, apparently as a result of the appearance of a certain fraction of ionic binding, increasing in proportion the reduction of nitrogen content within the limits of the regions of homogeneity. The latter is connected with the force of Me-Me bonds, the localization on them of a considerable part of the valence electrons, the decrease in the overlapping of the bands of valence electrons of the metal and the nitrogen and by corresponding appearance of energy gaps. The variation in the electric resistance of titanium and zirconium nitrides in the regions of homogeneity (Fig. 5) also differs from the course of resistance of corresponding carbides, being nonlinear. The appearance of an energy gap in the lattice of titanium nitride with incomplete nitrogen content, assumed in [822, 823], is confirmed by the variation in electric resistance at high temperatures (Fig. 6) [145]. Titanium

nitride with a nitrogen content, close to stoichiometric, reveals a linear increase in electric resistance with temperature with a decrease in nitrogen content of up to 48.4 at. %; maximum of resistance appears at 1800°C. With a further reduction in nitrogen content the resistance increases with the simultaneous displacement of the maximum into the region of lower temperatures. The width of the energy gap with a decrease in nitrogen content is increased. For titanium and zirconium nitrides with the decrease of nitrogen content in them within the limits of the regions of homogeneity an increase occurs in the width of the forbidden zone (see Table 6) [832].

Table 6. The composition and electrical properties of titanium and zirconium nitrides in the region of their homogeneity.

System	N content at. %	Specific electrical resistance ρ, $\mu\Omega\cdot$cm	Hall coefficient $R \cdot 10^4$ cm^3/c	Coefficient of thermo-emf α, μV/deg	Width of the forbidden zone ΔE, eV
Ti—N	35,8	112,5	—	—	0,77
	38,6	92	2,5	0,5	0,61
	41,0	60,5	1,5	—1,88	—
	43,4	50,5	0,9	—3,6	0,40
	48,2	28	—0,60	—7,1	—
	49,8	28	—0,67	—7,3	0,0
Zr—N	34,3	182	1,75	—2,4	1,59
	40,3	190	5,5	—0,98	0,73
	43,3	75	1,2	—4,0	0,50
	45,0	58	—1,4	—5,4	—
	46,8	37	—1,45	—7,7	0,29
	48,2	30	—1,4	—7,5	—
	48,9	28,5	—1,3	—7,4	0
	49,8	28	—1,3	—7,3	0

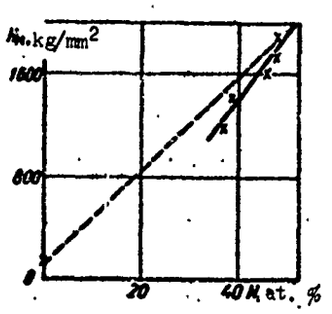

Fig. 4. The concentration dependence of microhardness in a region of homogeneity Ti-N.

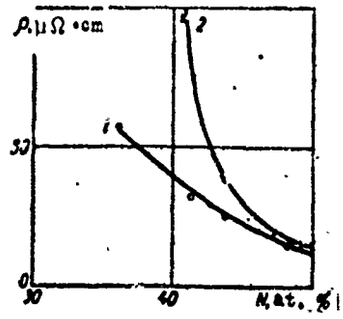

Fig. 5. The variation in the electric resistance of titanium and zirconium nitrides in regions of homogeneity: 1 – Zr-N; 2 – Ti-N.

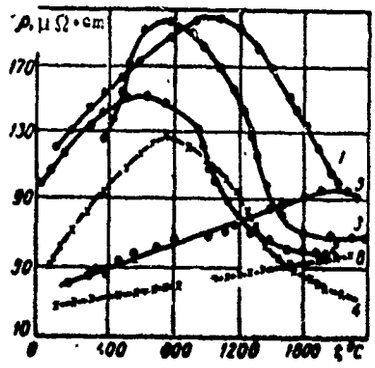

Fig. 6. The concentration-temperature dependence of the electrical resistance of titanium nitride in the region of homogeneity: 1 – 36.6; 2 – 38.6; 3 – 41.0; 4 – 43.4; 5 – 48.4; 6 – 49.8 at. % of N.

The width of the forbidden zone of titanium and zirconium nitrides varies linearly with an increase in the nitrogen content (Fig. 7.). A certain deviation from linearity for the nitrogen content below 40% is explained by the slight contamination by oxygen, the atoms of which can occupy free sites in the lattice of the unsaturated nitride. This assumption is confirmed by the presence of the impurity nature of the electroconductivity for ZrN with 34 at. % of N, whereas with other nitrogen contents this is not observed. It is necessary to note that the value of the forbidden zone and the rate of its variation for zirconium nitride is greater than for nitride of titanium which is connected with the great weight of the d^5-configurations for zirconium and the greater localization of electrons on the Zr-Zr bonds than on the Ti-Ti bonds.

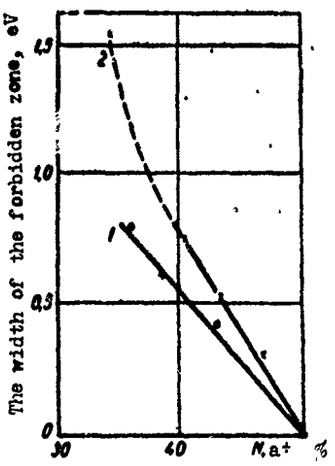

Fig. 7. The concentrational dependence of the variation of the width of the forbidden zone in the region of homogeneity: 1 — Ti-N; 2 — Zr-N.

In Fig. 8 the variation in the Hall coefficient and thermo-emf of titanium and zirconium nitrides in the region of homogeneity is shown.

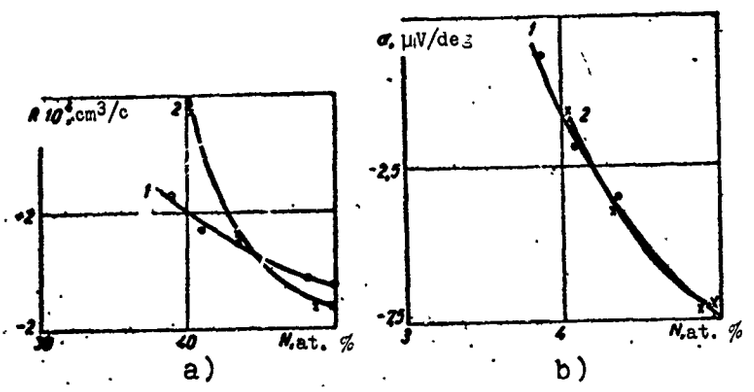

Fig. 8. Variation of the Hall coefficient (a) and the coefficient of thermo-emf; (b) of titanium and zirconium nitrides in the region of homogeneity: 1 — Ti-N; 2 — Zr-N.

Whereas the majority of transition-metal nitrides with a saturated nitrogen content possesses metallic properties, in chromium nitride CrN semiconductor properties are clearly expressed [326-328]. Nevertheless this nitride at low temperatures also has metallic (Fig. 9, section ab), with an increase in temperature — impurity

(section bc) and subsequently – intrinsic conductivity (section cd), characteristic for semiconductors. Probably, at increased temperatures the excitation of nitrogen states occurs and the transfer of one electron of a nitrogen atom to a chromium atom with the formation by chromium of stable d^5s^2-configurations, and by nitrogen of sp^3-configurations with a corresponding energy gap between them. At the same time nitride Cr_2N is not a semiconductor, apparently, in connection with the fact that chromium atoms form a great statistical weight of $d^{10}s^2$-configurations, and the nitrogen electron liberated accomplished metallurgical conductivity.

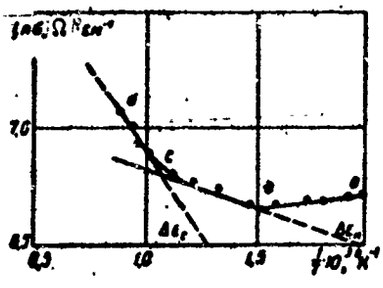

Fig. 9. The temperature dependence of the electric conductivity of CrN.

With the replacement in titanium nitride of a part of the nitrogen atoms by oxygen atoms (with ∿25-25 mole % of TiO) a minimum magnitude of resistance, Hall coefficient (Table 7) and thermo-emf is attained [174] with the preservation of the metallic nature of the conductivity. Upon heating a transition from metallic conductivity to semiconductor conductivity occurs; the temperature of such transition for all TiO contents is approximately identical and is about 1200°C [818]. The width of the forbidden zone for them is also identical and is 4.8-5 eV which is characteristic for ionic compounds, for which $\Delta E \approx 5$ eV. It is assumed that in the presence of oxygen the atoms of nitrogen and oxygen will mainly form s^2p^6-configurations, diverting to them the nonlocalized electrons of the titanium atoms, which in this case acquire a d^0-configuration, i.e., typically ionic compounds will be formed.

Table 7. Electrical properties of alloys of TiN-TiO.

Composition, mol. %		Specific electric resistance ρ, μΩ·cm	Hall coefficient R·10⁴, cm³/c	Coefficient of thermo-emf, α, μV/deg
TiN	TiO			
100	0	26	−0,67	−9,2
90	10	17,9	−0,4	−7,1
79,6	20,4	13,1	−0,17	−6,4
73,1	26,9	11,3	−0,48	−0,75
65	35	12,1	−0,82	—
62,7	37,3	12,7	−1,36	−8,6
47,6	52,4	14,2	−1,64	—
46,7	53,3	—	−1,70	−13,4
46	54	14,3	−2,02	—
41,8	58,2	27	−2,61	—

In work [825] the temperature dependence of electrophysical properties of titanium and vanadium nitrides of saturated composition was investigated. The electric resistance and the thermo-emf vary linearly with temperature which testifies to metallic conductivity, although of a mixed type.

The great magnitudes of the coefficients of thermo-emf in the whole temperature interval of the measurements also confirm the metallic nature of their electric conductivity. Like metals, the dependence of the specific electric resistance of these compounds on temperature can be described by a common expression of the type $\rho = \rho_0 \times (1 + \alpha t)$, where α is the temperature coefficient of electric resistance, ρ_0 is the magnitude of electric resistance at 0°C. An analogous expression can be used to describe the temperature dependence of thermo-emf $\varepsilon = \varepsilon_0 \times (1 + \beta t)$. Corresponding data are given in Table 8.

Table 8. The temperature dependence of certain electrophysical properties of titanium and vanadium nitrides of saturated composition.

Nitride	ρ_0, μΩ·cm	$\alpha \cdot 10^4$, deg^{-1}	temperature interval of application of ρ_0 and α, °C	ε_0, μV·deg	$\beta \cdot 10^4$, deg^{-1}	temperature interval of application of ε_0 and β, °C
TiN	24	4,4	0—1200	−3,7	2,06	280—1200
VN	88	0,7	0—1200	−6,2	1,16	280—1200

A comparison of the Mott [826] values $\sigma/M\theta^2$, (M is the molecular weight, θ is characteristic temperature), carried out for metallic titanium and different titanium and vanadium compounds, shows that for titanium and its diboride TiB_2 the temperature dependence $\sigma/M\theta^2$ is analogous, and for TiC and TiN it rather greatly differs from them (Fig. 10). This indicated deviation in the character of the bonding in TiC and TiN as compared to metallic titanium. The small value of the temperature coefficient of electric resistance for vanadium nitride (0.7 deg^{-1}) is explained by the possibility of the formation by the vanadium atoms of a high statistical weight of d^5-configurations due to the attraction of the electrons of the nitrogen atoms, and by the nitrogen atoms – of the correspondingly high statistical weight of sp^3-configurations, which are difficult to excite with an increase in temperature. The low value of the temperature coefficient of the electric resistance of vanadium nitride is connected with the high transition point to superconductivity (7.50°K), which is also caused by the "inertness" of the walls of the energetic "channels", formed by atoms with a high statistical weight of stable configurations.

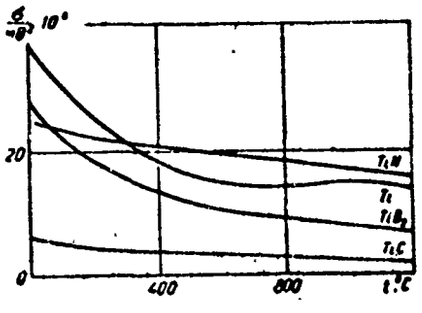

Fig. 10. The temperature dependence of the indicated electrical conductivity of titanium and its compounds with nitrogen, boron and carbon.

The values of the thermoelectric quality factors $Z = \alpha^2/\rho\lambda$ (α is thermo-emf, ρ is specific electric resistance, λ is thermal conductivity) of transition-metal carbides in comparison with the nitrides are given in Table 9. For the majority of nitrides the quality factor is small (10^{-7} to 10^{-5} deg^{-1}) which agrees with the

metallic character of their electrical conductivity. A higher Z value is observed only for CrN which is caused by its semiconductor nature. From Fig. 11 [827] it is clear that with the increase of number $\xi = 1/Nn$ or with the decrease in the statistical weight of the d^5-configurations of the atoms of a transition metal the thermoelectric quality noticeably increases which is caused by the increase in the electronic contribution to thermal conductivity (and by the decrease in the lattice contribution, caused by the electrons, localized in the stable configurations). It is interesting that for a scandium-metal nitride, for which the formation of a high statistical weight of d^0-states and a small statistical weight of d^5-states and strong delocalization of the valence electrons are characteristic – the quality factor approaches that for semiconductor chromium nitride. Obviously, this is due to different causes and in general characterized scandium nitride as a typical semimetal.

Table 9. Coefficients of the thermoelectric quality of refractory carbides and nitrides.

Compound	z, deg^{-1}	Compound	z, deg^{-1}
TiC	$2{,}1\cdot10^{-5}$	WC	$0{,}9\cdot10^{-4}$
ZrC	$1{,}1\cdot10^{-5}$	V_2C	$3{,}0\cdot10^{-6}$
HfC	$1{,}0\cdot10^{-5}$	$ScN_{0,98}$	$0{,}8\cdot10^{-4}$
$VC_{0,88}$	$0{,}9\cdot10^{-6}$	$TiN_{0,98}$	$1{,}2\cdot10^{-5}$
$NbC_{0,99}$	$2{,}1\cdot10^{-6}$	$ZrN_{0,98}$	$4{,}0\cdot10^{-6}$
TaC	$5{,}0\cdot10^{-6}$	$HfN_{0,86}$	$1{,}2\cdot10^{-6}$
Cr_3C_2	$2{,}2\cdot10^{-6}$	$VN_{0,93}$	$2{,}2\cdot10^{-6}$
Cr_7C_3	$3{,}1\cdot10^{-6}$	$NbN_{1,00}$	$3{,}1\cdot10^{-7}$
$Cr_{23}C_6$	$3{,}0\cdot10^{-7}$	$TaN_{1,01}$	$2{,}3\cdot10^{-7}$
Mo_2C	$7{,}6\cdot10^{-6}$	$CrN_{0,93}$	$1{,}4\cdot10^{-4}$

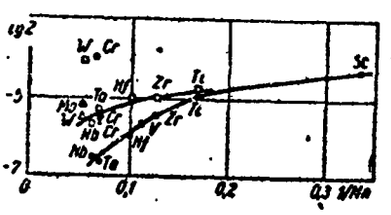

Fig. 11. The dependence of the quality factors of transition-metal on the number 1/Nn: □ are MeC carbides; ○ are MeN nitrides; △ is W_2C; ▲ is Mo_2C; ▽ is Cr_7C_3; × is Cr_3C_2.

Thermionic emission properties. The work function in the case of thermionic emission is determined by the relationship of the statistical weights and the energetic characteristics of localized and nonlocalized parts of valence electrons, being increased with an increase in the weight and energetic stability of stable configurations of electrons localized near atoms [845]. The work function of transition-metal nitrides (Table 10) increases from titanium nitride to tantalum and niobium nitrides (Fig. 12) [170, 252, 846-849].

Table 10. Thermionic emission of nitrides.

Nitride	Work function ϕ, eV	Richardson's constant A, $a/cm^2\ °K^2$	Notes	Literature
TiN	2.92	120.4	-	[170]
	3.75	-	Effective work function at 2000°K, measured in powder	[846]
ZrN	2.92	120.4		[170]
	3.90	-	Effective work function at 1900°K, measured in powder	[846]
VN	3.56	-	Effective work function at 1600°K	[252]
NbN	3.92	-	The same at 1950°K	[846]
TaN	4.00	-	The same at 1600°K	[252]
ThN	3.1	-	Photoemission	[848]
UN	-	-	The temperature dependence of effective work function is given by the expression $\varphi_T = 3{,}1 + 2{,}1 \times 10^{-4}T$	[849]

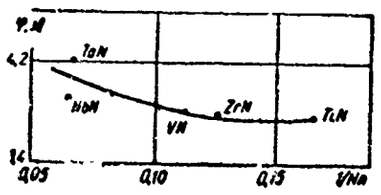

Fig. 12. The dependence of the work function in the case of thermoionic emission of transition-metal nitrides at a temperature of 1700°C on the number 1/Nn.

A comparison of the values of the work function of nitrides and carbides shows that in the latter case they are smaller which is explained by the formation in nitrides along with sp^3-configurations of nitrogen atoms (with the corresponding liberation of an electron and its transfer to an aggregate), also of s^2p^6-configurations, the formation of which is connected with the considerable localization of the valence electrons of both the transition metals, and also of nitrogen. Transition-metal nitrides have as yet not found practical application in cathode electronics, since their thermoelectric properties are not very high and, furthermore, they dissociate in a vacuum upon heating.

Superconductivity. It has been established now that the greater part of transition-metal nitrides is superconductors [275, 304, 1001, 1013]. The corresponding data on the superconductivity of nitrides are presented in Table 11.

Table 11. Superconductivity of nitrides.

Nitride	$T_к$, °K	Nitride	$T_к$, °K
ScN	$\leqslant$1,40	TaN	$\leqslant$1,20
YN	$\leqslant$1,40	Ta_2N	$\leqslant$1,20
TiN	4,85	CrN	$\leqslant$1,28
ZrN	8,90—10,7	MoN	12,0
HfN	6.20	Mo_2N	5,0
VN	8,20	W_2N	$\leqslant$1,28
NbN	15,60	Th_3N_4	$\leqslant$1,20
Nb_2N	$\leqslant$1,20	UN	$\leqslant$1,20

It is noted that T_k in general increase with the increase in the weight of stable d^5-configurations of the atoms of corresponding transition metals (for mononitrides), with the exception of tantalum, chromium and tungsten nitrides. With a decrease in the relative nitrogen content in the nitride phase T_k drop. If it is considered that the conditions of superconductivity, on the one hand, is the formation by atoms of "energetic channels", the stability of the "walls" of which is ensured by the strong localization of electrons

in stable configurations, which possess a reduced capacity for diffusion of conduction electrons, and on the other hand, the formation by conduction electrons of Cooper pairs, also possessing a reduced capacity for diffusion, then the increase of T_k with the increase of the weight of stable configurations in a metal is well explained. In the same way the high T_k of nitrides as compared to carbides, borides and other similar compounds are explained in general [275]. Actually, in the case of the formation of nitrides of metals of group IV there is a high number of nonlocalized electrons, which are partially localized on the s^2p^6-configurations of nitrogen and the d^5-configurations of the metal. With the transition to metals of groups V and VI the localization of the valence electrons near atoms of metals is higher which causes the formation of a high statistical weight of d^5-configurations of the metal and sp^3-configurations of nitrogen. With this the high stability of the "walls" is ensured of the energy gap [876] with a moderate concentration of carriers. In case of tantalum, chromium and tungsten such "walls" will also be formed, but with the simultaneous formation of a reduced number of current carriers which leads to the reduction of T_k. Therefore of great interest is the high T_k of solid solutions of NbN-NbC, for which with the composition $(NbC)_{0.28}$-$(NbN)_{0.72}$ the point of transition is 17.9°K [828]. Also the high statistical weight of d^5-configurations of niobium atoms, the sp^3-configurations of carbons and nitrogen atoms along with the optimum concentration of current carriers is ensured. According to the theory of Bardeen, Cooper and Schrieffer, the temperature of transition to superconductivity is determined by the expression

$$kT_k = 1{,}14\,(\hbar\omega)_{cp} \exp(-1/N(0)\cdot V),$$

where k is the Boltzmann constant; $(\hbar\omega)_{cp}$ is the average energy of phonons, scattering electrons near the Fermi surface (proportional to the Debye temperature); N(0) is the normal density of the electronic energy state near the Fermi surface; V is the constant of electron-phonon interaction. It is possible to affirm that transition temperature to the superconducting state is mainly determined by the factor

N(0)·V or, considering the approximate constancy of V, by the density of the states. In work [828] correspondence was actually shown between T_k and the density of the states for a number of nitrides, and also for solid solutions of NbC-NbN (Fig. 13). The best results were obtained by the correlation T_k with the theoretical density curves of the states, obtained by Biltz, and also by Ern and Soitendik [Translator's Note: This name spelled two different ways in foreign document (typographical error) See Fig. 13]. The authors assumed that the main role in the formation of the properties of substances belongs to the highly localized compounds between the metal and nonmetal atoms, i.e., covalent bonds.

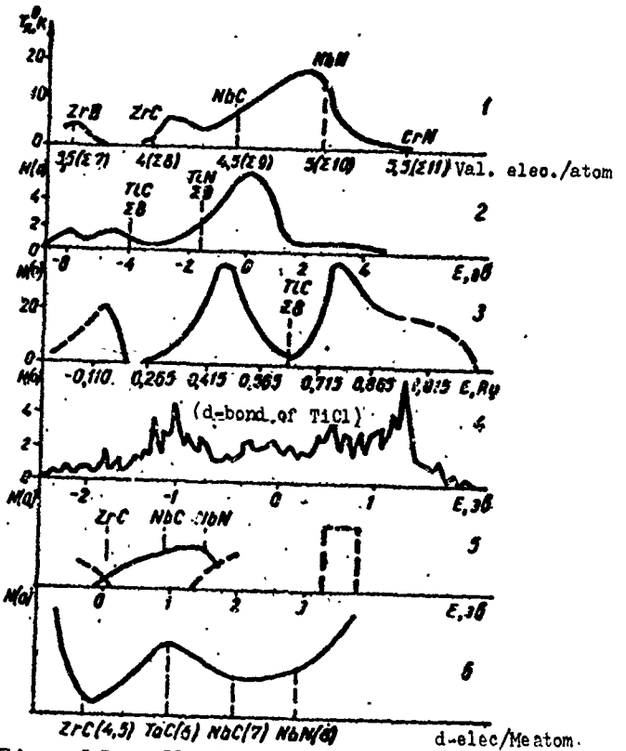

Fig. 13. Variation in the critical transition temperature to superconductivity T_k in the series ZrB-NbC-NbN-CrN: 1 – analytic curves of the variation in the density of states; 2 – according to Biltz; 3 – according to Ern and Svitenlik; 4 – according to Costa and Conte; 5 5 – according to Popper, 6 – according to Dempsey.

With the variation in nitrogen content in the region of homogeneity T_k varies, and for zirconium nitride – monotonically (Fig. 14) [275, 1069], and for niobium nitride the maximum T_k corresponds to the nonstoichiometric composition NbN (Fig. 15). The decrease in T_k with a reduction in the nitrogen content in the region of homogeneity or a definite part of it agrees with the decrease in T_k in the nitride phases with the reduction in them of the nitrogen content (for example MoN and Mo_2N). This is explained by the strengthening of the Me-Me bonds and by localization on them of a very large part of the valence electrons with a corresponding reduction in the concentration of conduction electrons and by the appearance of energy gaps. In particular, chromium nitride is a semiconductor. The energy gaps acquire great importance in tantalum and tungsten nitrides, and also in the seminitrides Nb_2N and Mo_2N. In the case of the variation of T_k in the region of homogeneity of niobium nitride the reduction in T_k starting from a certain nitrogen content toward stoichiometric composition (in region of from 0.95 to 1.00 niobium in NbN) can be explained by the appearance with these nitrogen contents of strong Me-Me and N-N bonds and by the beginning of the formation of an energy gap.

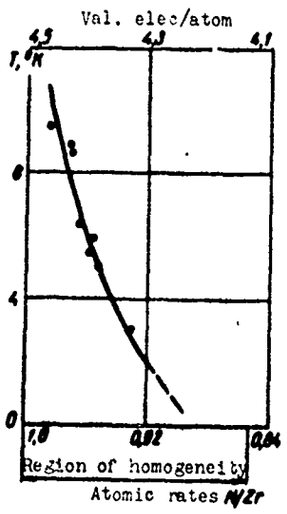

Fig. 14. The variation of the transition to superconductivity in the region of homogeneity of ZrN.

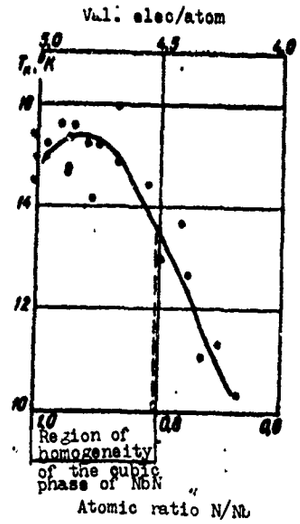

Fig. 15. Variation of the transition point to superconductivity in the region of homogeneity of NbN.

The authors [1001] investigated the concentration dependence of T_k in the regions of homogeneity of titanium TiN_{1-x} and vanadium VN_{1-x} nitrides and determined the value of T_k for yttrium mononitride. Values of T_k in the regions of homogeneity of titanium and vanadium nitrides, as also for zirconium and niobium nitrides, drop with a decrease in the nitrogen content.

Magnetic properties. The first investigation of the magnetic properties of the nitrides of certain transition metals was conducted in [829]. It showed the rather weak paramagnetism of titanium and zirconium nitrides (χ_M for TiN + $48 \cdot 10^{-6}$, for ZrN + $60 \cdot 10^{-6}$). It was determined that chromium nitride is a ferromagnetic material [331], the nitrides Mn_4N, Mn_5N_2, Fe_4N are highly paramagnetic material with effective magnetic moments respectively of 1.2; 3.94; 2.22 Bohr magnetons [140], the uranium nitrides ar very weak magnetic materials with a magnetic susceptibility of: UN + 7.73; U_2N_3 + 13.17 [508]. In a number of lanthanide mononitrides the magnetic susceptibility increases [478]:

LaN	CeN	PrN	NdN
+60	+296	+4460	+5850

Upon the dissolution titanium carbide in titanium nitride the magnetic susceptibility of the alloy sharply decreases [830], as is shown in Fig. 16.

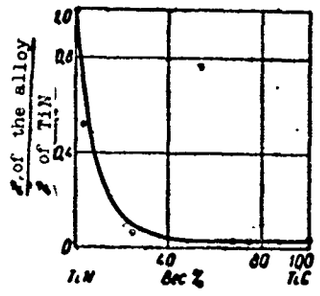

Fig. 16. Magnetic susceptibility of TiN-TiC alloys.

Thus, at the present time no considerable experimental material on the magnetic properties of transition-metal nitrides has not been accumulated and no interpretations of the available data have been proposed. It is only possible to note that the paramagnetism of the lanthanide nitrides increases with an increase in the statistical weight of the stable f^7-configurations of the lanthanide atoms. The decrease in the magnetic susceptibility of titanium nitride upon the dissolution in it of the carbide can be connected with the reduction in the statistical weight of the s^2p^6-configurations and the increase in the statistical weight of the sp^3-configurations with the simultaneous rather high delocalization of the valence electrons of both titanium and nitrogen.

Certain data on the magnetic properties uranium and plutonium nitrides at low temperatures are given in [831].

Thermal properties. It was shown above that for the majority of nitrides the prevalent role is played by the electronic component of thermal conductivity, with the exception of chromium, tantalum and vanadium nitrides, for which due to the considerable localization of valence electrons on covalent bonds the lattice component of thermal conductivity prevails.

The thermal expansion of transition-metal nitrides was investigated in [781, 225] (Table 12).

Table 12. Thermal expansion of transition-metal nitrides.

Nitride	Temperature interval, °C	Coefficient of thermal expansion $\alpha \cdot 10^6$, deg^{-1}	Porosity of the sample, %	Literature
TiN	20—270	8,87±0,4	—	[781]
$TiN_{0,98}$	20—1100	9,5	11	[225]
ZrN	20—270	10,2±0,5	—	[781]
$ZrN_{0,92}$	20—1100	7,24	4,4	[225]
$HfN_{0,86}$	20—1100	6,9	3,1	[225]
VN	17—190	8,35±0,74	—	[781]*
$VN_{0,93}$	20—1100	8,1	10	[225]
$VN_{0,93}$	20—1100	9,2	4,5	[225]
NbN	20—270	10,1±0,2	—	[781]*
$NbN_{0.5}$	20—1000	3,26	9,2	[225]
$NbN_{1,0}$	20—1000	10,1	3,7	[225]
$TaN_{0,45}$	20—1000	5,2	5,4	[225]
$TaN_{1,01}$	20—790	3,6	7,8	[225]
$CrN_{0,49}$	20—1100	9,41	6,1	[225]
$CrN_{0,92}$	20—800	2,3	9,9	[225]
	850—1040	7,5		[225]
$MoN_{0,5}$	20—790	4,5	12,3	[225]
	20—1100	6,2		[225]

*Contaminated with carbon.

The rather high values of the coefficient of thermal expansion of nitrides differ little from the values the coefficient of thermal expansion of the corresponding transition metals [781]. This indicates that the bonding forces in nitrides of the MeN type insignificantly exceed the bonding force in the transition metals and are 2-3 times less than the bonding forces in the corresponding carbides. It is obvious that the loosening effect of the nonlocalized part of the valence electrons is responsible for this. There is observed, although not clearly expressed, a decrease in the coefficient of thermal expansion of nitrides with a growth in the localization of valence electrons in the d^5-configurations of a metal and the sp^3-configurations of nitrogen.

The thermal stability of nitrides at high temperatures has been investigated in many works. In Fig. 17 there are given, according to the data of [833], analytic curves of the elasticity of the

dissociation of nitrides at various temperatures. The authors [834] investigated the dissociation of nitrides in a vacuum of 10^{-4} mm Hg; the results are shown in Fig. 18. A detailed survey of the stability of nitrides in a vacuum is given in monograph [835].

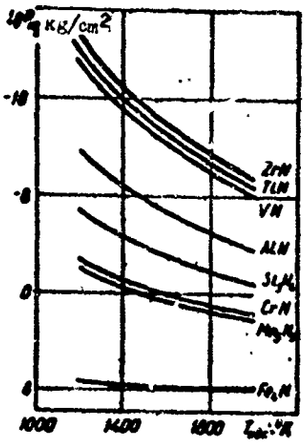

Fig. 17. Analytic curves of the elasticity of dissociation of nitrides [833].

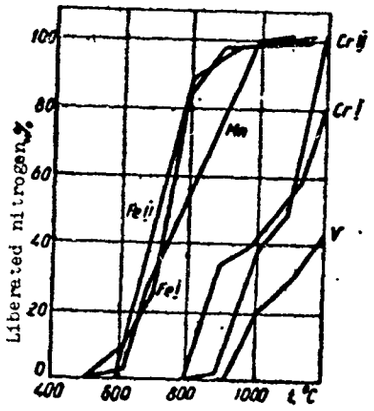

Fig. 18. The behavior of certain nitrides in a vacuum.

Investigations of the vaporization of nitrides in a vacuum showed, that nitrides dissociate into metal and nitrogen

$$MeN_{(тв)} = Me_{(тв)} + \frac{1}{2}N_2. \qquad (I.1)$$

In work [203] the vaporization rates and the vapor pressures of titanium and zirconium nitrides were determined. At temperatures

of 2000-2240°K the vaporization rate of titanium attains a considerable magnitude, therefore th. dissociation pressure was calculated in this way

$$TiN_{(тв)} = Ti_{газ} + \frac{1}{2}N_2. \qquad (I.2)$$

Zirconium nitride under the same conditions dissociates in this way (I.1). Data on the vaporization rate and the dissociation pressure of TiN and ZrN are given in Table 13.

Table 13. Vaporization rate and dissociation pressure of TiN and ZrN.

TiN			ZrN		
T, °K	$G \cdot 10^3$, g/cm²·s	$P_{N_2} \cdot 10^6$, at	T, °K	$G \cdot 10^3$, g/cm²·s	$P_{N_2} \cdot 10^6$, at
1987	1,510	0,650	2236	0,534	0,915
2017	1,972	0,854	2259	1,299	2,397
2050	3,129	1,366	2318	2,979	5,[illegible]33
2058	3,360	1,469	2333	2,714	4,977
2155	15,963	7,146	2344	3,020	5,536
2157	20,510	9,178	2451	14,981	28,96
2212	33,254	15,68	2466	16,127	31,04
2241	70,555	32,21			

From Table 14 [74] it is clear that the dissociation of nitrides is hampered by a decrease in the localization of valence electrons into stable configurations and is substantially facilitated with high localization, extending as far as the appearance of energy gaps between the metal atoms and the nitrogen atoms. For semiconductor nitrides of chromium, molybdenum and tungsten the elasticity of dissociation is greatest at minimum temperatures. It is noted that the relatively high elasticity of dissociation of vanadium nitride, which can be compared with the low thermal coefficient of electric resistance of this nitride, the relatively high transition temperature of transition to superconductivity and other characteristics, indicating the high statistical weight of the stable configurations of vanadium and nitrogen atoms in this compound and the low weight of the nonlocalized part of the valence electrons.

Table 14. Elasticity of the dissociation of nitrides [74].

Nitride	Temperature (°C) at a pressure of 1 mm Hg	10^{-1} mm Hg	10^{-2} mm Hg	10^{-3} mm Hg
ScN	1880	1734	1607	1495
YN	1990	1838	1704	1587
TiN	2912	2689	2489	2331
ZrN	2603	2390	2205	2046
VN	1242	1127	1024	933
NbN	1946	1770	1620	1491
TaN	1921	1746	1599	1460
CrN	719	646	582	533
Mo_2N	329	283	243	209
W_2N	344	296	256	221
Th_3N_4	2401	2206	2037	1890
U_2N_3	2267	2070	1950	1753
LaN	2010	1855	1721	1602
CeN	2196	2029	1884	1756

Optical properties. The optical properties of transition-metal nitrides have been little studied. The available data [340] on the emission coefficient of nitrides at a wavelength of emitted light of λ = 650 nm are given in Table 15.

Table 15. Emission coefficients of transition-metal nitrides.

Nitride	800°C	900°C	1000°C	1100°C	1200°C	1300°C	1400°C	1500°C	1600°C	1700°C	1800°C	1900°C	2000°C
TiN	0,82	0,81	0,81	0,80	0,80	0,80	0,79	0,79	0,79	0,79	0,78	0,78	0,78
ZrN	0,73	0,73	0,73	0,74	0,74	0,75	0,75	0,75	0,75	0,75	0,76	0,76	0,76
HfN	0,84	0,84	0,84	0,84	0,84	0,84	0,84	0,84	0,84	0,84	0,84	0,84	—
V_2N	0,82	0,82	0,82	0,82	0,82	0,82	0,82	0,82	0,82	—	—	—	—
VN	0,77	0,77	0,77	0,77	0,77	0,77	0,77	0,77	0,77	0,77	0,77	0,77	0,77
Nb_2N	0,82	0,82	0,82	0,82	0,82	0,82	0,82	0,82	0,82	0,82	—	—	—
NbN	0,83	0,83	0,83	0,83	0,83	0,83	0,83	0,83	0,83	0,83	0,83	0,83	0,83
Ta_2N	0,83	0,83	0,83	0,83	0,83	0,83	0,83	0,83	0,83	0,83	—	—	—
TaN	0,79	0,79	0,79	0,79	0,79	0,79	0,79	0,79	0,79	0,79	0,79	0,79	0,79
Cr_2N	0,69	0,69	0,69	0,69	0,69	0,69	0,69	0,69	0,69	—	—	—	—
CrN	—	—	—	0,60	0,58	0,55	0,53	0,51	0,48	0,46	0,44	0,42	0,38

The diffusion of nitrogen in transition metals. The obligatory condition of diffusion is the formation as a result of the diffusion process of a system, stabler in an energetic regard than the mixture of the initial components, i.e., possessing less free energy. This

condition can be fulfilled, if as a result of diffusion the statistical weight of the atoms, possessing stable configurations of a localized part of the valence electrons, increases. With the diffusion of nitrogen either the transfer by its atoms of one electron to the metal atoms with the formation of an sp^3-configuration is possible or the acceptance by the nitrogen atoms of the valence electrons of the metal with the formation of an s^2p^6-configuration. Since part of the nitrogen atoms can give up a highly mobile electron, then the activation energy of the diffusion of nitrogen in the transition metals is somewhat higher than the activation energy with the diffusion of carbon in the same metals, but lower than boron. This is explained by the fact that in the latter case the most energetically efficient state of boron atoms is their unification with the liberation of a part of the electrons and with the formation of sp^3-configurations (Table 16).

Table 16. Activation with the diffusion of certain nonmetals in transition metals, kJ/mole [850].

Metal	Boron	Carbon	Nitrogen	Oxygen
Ti	128,12	79,97	141,51	140,26
Zr	144,44	171,66	164,12	124,77
Hf	—	—	238,65	233,83
Nb	247,02	133,98	161,6	115,87
Ta	200,97	104,67	184,22	121,42
Cr	—	117,23	43,63	—
Mo	184,4	347,5?	—	—
W	—	257,49	—	—

The diffusion rate usually increase with an increase in activation energy, since the high values of activation energy correspond to the formation on the surface of a not very high statistical weight of atoms with stable configurations and to the relative ease of their disturbance for the continuation and development of the diffusion process.

In practice at low temperatures solid solutions of nitrogen in metals will be formed; at higher temperatures diffusion acquires

a reaction character, i.e., it is accompanied by the formation of nitride phases which are frequently used for the creation of nitride coverings on metals.

Tensile properties. The strength of transition-metal nitrides at normal and high temperatures has been little investigated [140, 147, 851]. Between microhardness and the factor of Lindemann's equation, determining the frequency of the oscillations of linear oscillators, there is a certain correlation (Fig. 19) [852]. This is apparent, proceeding from the closeness of the processes, occurring during melting and the measurement of hardness, to which in his time Born indicated, and in the application of interstitial phases – in [852, 853]. In work [858] an attempt is made to connect hardness with the energies of the atomization and the complete and free specific surface energies. The hardness of the lowest nitride phases is substantially higher than the hardness of mononitrides which can be explained by analogy with the concepts of [854, 781] by the essential strengthening of the Me-Me compounds with a decrease in the relative number of interstitial atoms of nitrogen in phases of saturated composition. In work [147] it was demonstrated that with a decrease in the nitrogen content within the limits of the region of homogeneity of the nitride phases of transition metals hardness is reduced. The decrease occurs at a greater rate than for carbides which is explained by appearance for the nitrides of a fraction of an ionic bond, increased with a reduction of the nitrogen content within the limits of the region of homogeneity, i.e., with an increase in the localization of electrons on the Me-Me bonds and with an increase in the statistical weight of the s^2p^6-configurations of nitrogen atoms. The decrease in hardness is accompanied by the appearance and the increase in the energy gaps between states of the metal and nitrogen atoms that externally appears in the increase in the width of the forbidden zone.

For the phases of saturated composition with respect to the nitrogen content hardness regularly decreases with an increase in

the weight of the stable configurations of transition-metal atoms (Fig. 20). With this a reduction in the statistical weight of s^2p^6-configurations occurs and an increase in the statistical weight of the sp^3-configurations of the nitrogen atoms, i.e., a simultaneous increase in the symmetry of the distribution of the electron density to which a reduction in hardness always corresponds [851]. It is necessary to note that the factor of symmetry is stronger than the weight factor of nonlocalized electrons, thus, for example, fo- titanium nitride, in spite of the great weight of the nonlocalized electrons and the strong lossening of the lattice caused by them, the hardness is even greater due to the acute asymmetry of the distribution of the localized electrons.

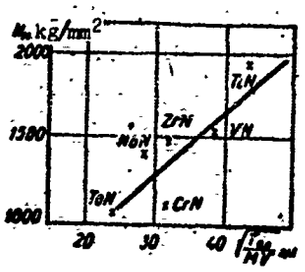

Fig. 19. The relationship between the microhardness numbers of transition-metal nitrides and the factor of Lindemann's equation.

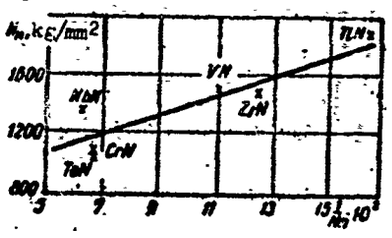

Fig. 20. The dependence of the microhardness of transition-metal nitrides on the criterion ξ.

The presence of a relatively high weight of nonlocalized electrons in the transition-metal nitrides, participating in the statistical exchange with localized electrons, determines not only their lower hardness than the other analogous compounds (carbides, borides, silicide), but also their lower fragility [855, 856]. In this case this is absolutely analogous to reducing the fragility

and increasing the plasticity in the C series (diamond) – Si-Ge-Sn (white) – Pb. In this series the localization of valence electrons on stable sp^3-configurations is reduced; the configurations determining the rigid, directional bonds, and the weight of the nonlocalized electrons is increased, which ensure bonding with the localized electrons, entering into stable configurations and, consequently, with the cores of the atoms. In other words, for transition-metal nitrides there exists the great capacity of the breaking of the interatomic bonds, i.e., without destroying the material.

The study of the abrasive capacity of certain nitrides carried out by us showed that the abrasive capacity decreases in proportion to the decrease in hardness, rather noticeably reducing with this the abrasive capacity of the carbides and especially of the borides of those same metals [1068].

Transition-metal nitrides are destroyed by ultrasound [ultrasonic vibrations] [776].

Nonmetal nitrides. Nonmetal compounds with nitrogen are characterized mainly by a covalent type of chemical bond and by physical properties of a nonmetallic or semimetallic nature corresponding to this type. The greatest interest is being manifested in bonds of nonmetals and semimetals of groups III and IV with nitrogen. Transition-metal compounds of group III with nitrogen are semiconductor compounds of the type $A^{III}B^{V}$. With their formation atoms of components A (A = B, Al, Ga, In, Tl), having in an isolated state an s^2p-configuration of valence electrons, acquire a stabler sp^2-configuration as a result an s → p-transition, and then, joining to themselves an electron of a nitrogen atom – quasi-stable sp^3-configuration, whereas a nitrogen atom, also losing electron, acquires an sp^3-configuration, [857]. Semicondutors of the type $A^{III}B^{V}$ are analogous in structure and properties to semiconductors of the carbon (diamond) group. Obviously, the stablest configurations of partners A and B should be possessed by the cubic boron nitride – borazon,

which causes the great width of its forbidden zone, its high hardness and melting point, and isolation of the stable configurations — disproportionation upon heating and incongruent melting. With the replacement of boron by aluminum and so forth, with the constant second component nitrogen, the hardness, melting point and width of the forbidden zone are regularly reduced (Table 17). Also the energy isolation of the configurations of atoms is reduced; so that, if BN upon heating is decomposed, then GaN vaporized molecularlly [616]. All A elements, except boron, form with nitrogen of compounds, possessing not a lattice of sphalerite, and würtzite, apparently, due to the sharp difference in the energetic stability of the corresponding electronic configurations. This results in the acceptor role of nitrogen with the completion of its electronic s^2p^3-configuration up to the stable state s^2p^6-formation of a high statistical weight of these states by both atoms (A and B).

Table 17. Physical properties of transition-metal nitrides of group III of the periodic system.

Nitride	Crystal structure	Melting point, °C	Width of the forbidden zone, eV	Hardness according to Mohs hardness scale
BN	Cubic type of sphalerite	3000	~10	10
AlN	Hexagonal type of würtzite	2200	3.8	9
GaN	The same	1500	3.25	-
InN	The same	1200	-	-

Considering the higher stability of the s^2p^6-configurations in comparison to sp^3, it is understandable, why compounds with the structure of würtzite a great width of the forbidden zone as compared to compounds, crystallized in the form of sphalerite, and also relatively high values of melting points and hardness (AlN, GaN, InN).

With the transition from nitrogen to phosphorus the sharp reduction in the stability of a possible s^2p^6-configuration leads to the giving up by the s^2p^6-configurations to component A of one electron, to the formation of sp^3-configurations by both atoms and accordingly – of the structure of sphalerite.

A definite correlation is observed between microhardness and the width of the forbidden zone of $A^{III}B^{V}$ semiconductors (Fig. 21), and also a correlation between melting point and microhardness (Fig. 22). It is noted that the smooth diminution in the hardness of compounds of boron, aluminum and indium is disturbed by the somewhat higher course of the microhardness of a number of gallium compounds, i.e., to the relatively smaller width of the forbidden zone of $A^{III}B^{V}$ gallium compounds there correspond the relatively higher values of microhardness than for compounds of other A metals. A similar departure is also observed for the melting points of compounds of gallium, which have relatively high values of melting points, as well as values of microhardness. An increase in the hardness and the melting point can be connected with the appearance for these compounds along with sp^3-configurations of also a definite statistical weight of configurations of s^3p^6 type. This, apparently, should become more pronounced for indium compounds. However due to the appearance for indium of a completely vacant 4f-shell the disturbance of sp-configurations is possible as a result of the partial transitions of valence electrons to 4f-states. For aluminum the formation of s^2p^6-configurations is most completely expressed for AlN, as was already noted above, in compounds of aluminum with P, As, and so forth. The transfer of electrons from Al to phosphorus and other B components is hampered as a result of the relatively close energy states of the sp-electrons of both components. For gallium, having a lower energy state of sp-electrons, the transfers from it of electrons to component B are resumed. Thus, the formation is possible by component atoms simultaneously of sp^3- and s^2p^6-electron configurations, the relationship of the statistical weights of which can oscillate over a wide range – from practically

100% of sp^3-configurations (and the formation of the structure of sphalerite) to practically 100% s^2p^3-configurations (with the formation of the structure of würtzite). Therefore for gallium atoms in its compounds of the $A^{III}B^V$ type a high statistical weight of s^2p^6-configurations is possible, and it is possible to expect polymorphous transformations for these compounds under certain conditions.

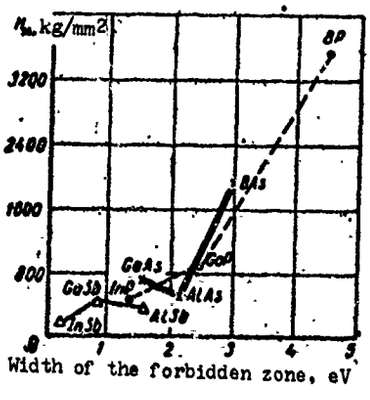

Fig. 21. The relationship between the microhardness and the width of the forbidden zone of semiconductors of the $A^{III}B^V$ type.

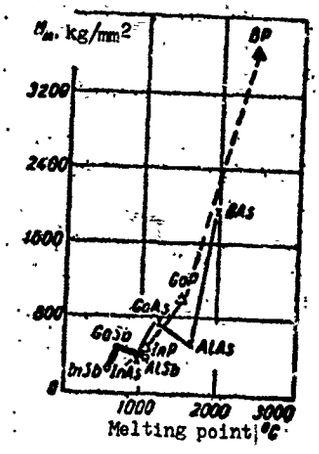

Fig. 22. The relationship between the microhardness and the melting point of semiconductors of the $A^{III}B^V$ type.

3. Thermodynamics of Nitrides[1]

The thermodynamic properties of nitrides are presented in reference books and survey works [47, 112, 862]. Therefore in this

[1]This section was written by R. F. Voytovich.

section the main attention is focussed on the relative thermodynamic stability of nitrides in various media, the determination of the temperature range of thermodynamic stability and the equilibrium values of the partial pressure of the nitrogen of nitrides, the possibility of achieving reactions between nitrides and other compounds, and also on an evaluation of the expected properties of the products of the reactions.

In Tables 18 and 19 the thermodynamic properties of certain nitrides are presented, and in Fig. 23 the dependence of the isobaric-isothermic potentials [Gibbs free energies] of the formation reactions of nitrides is presented.

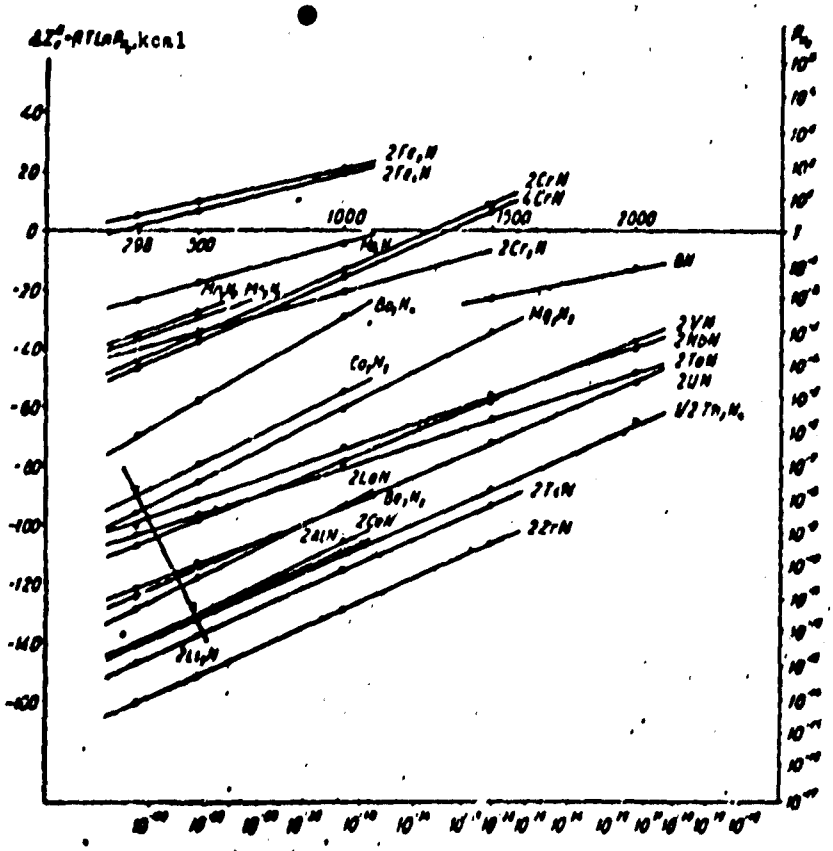

Fig. 23. The dependence of the isobaric-potential [Gibbs free energy] of formation reactions of nitrides on temperature.

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Table 18. Thermodynamic properties of nitrides.

Compound	ΔH°_{298} kJ/mole	ΔH°_{298} kcal/mole	S°_{298} J/mole·deg	S°_{298} cal/mole·deg	Phase	T_{tr}, °K	$-\Delta H_{tr}$ kJ/mole	$-\Delta H_{tr}$ kcal/mole	Heat capacity $C_p = a + bT + cT^{-2}$: a J/mole·deg	a cal/mole × deg	b·10³ J/mole·deg	b·10³ cal/mole × deg	c·10⁻⁵ J/mole·deg	c·10⁻⁵ cal/mole × deg	Temperature interval, °K
Li_3N	196,78	47,0	—	—	Solid	Decomposes	—	—	49,11	11,73	96,30	23,0	—	—	298—[illegible]
K_3N	73,69	17,6	—	—	»	—	—	—	—	—	—	—	—	—	—
Ca_3N_2	—74,53	—17,8	—	—	»	Decomposes	—	—	90,85	21,7	—	—	—	—	273—373
Ag_3N	—355,39	—61,0	—	—	»	»	—	—	—	—	—	—	—	—	—
Be_3N_2	563,96	134,7	50,24	12,0	»	2473	—	—	30,66	7,32	128,95	30,8	—	—	298—[illegible]
—	—	—	—	—	Liquid	Decomposes	—	—	—	—	—	—	—	—	—
Mg_3N_2	461,80	110,3	87,92	21,0	Solid (α)	823	0,46	0,11	96,96	20,77	46,892	11,20	—	—	298—[illegible]
—	—	—	—	—	Solid (β)	1061	0,92	0,22	84,089	20,07	44,631	10,66	—	—	[illegible]—1061
—	—	—	—	—	Solid (γ)	Decomposes	19,324	28,50	—	—	—	—	—	—	1061—[illegible]
Ca_3N_2	351,69	84,0	—	—	Solid	—	—	—	—	—	—	—	—	—	—
Cr_2N	439,61	105,0	106,34	25,4	»	1468	—	—	85,58	20,44	92,11	22,0	—	—	298—[illegible]
Sr_3N_2	391,05	93,4	123,51	29,5	»	1303	—	—	—	—	—	—	—	—	—
Ba_3N_2	363,83	86,9	152,40	36,4	»	Decomposes	—	—	—	—	—	—	—	—	—
Zn_3N_2	22,19	5,3	—	—	»	»	—	—	79,55	19,0	94,20	22,5	—	—	273—700
Cd_3N_2	—161,61	—38,6	—	—	»	»	—	—	—	—	—	—	—	—	—
[illegible]	284,70	68,0	37,68	9,0	»	2923	—	—	—	—	—	—	—	—	—
[illegible]	299,36	71,5	46,05	11,0	»	—	—	—	—	—	—	—	—	—	—
[illegible]	299,36	71,5	—	—	»	—	—	—	46,47	11,1	—	—	—	—	298
[illegible]	326,57	78,0	48,99	11,7	»	—	—	—	46,89	11,2	—	—	—	—	298
[illegible]	314,01	75,0	—	—	Solid	—	—	—	—	—	—	—	—	—	—
GdN	314,01	75,0	—	—	»	—	—	—	—	—	—	—	—	—	—
DyN	314,01	75,0	—	—	»	—	—	—	—	—	—	—	—	—	—
ErN	314,01	75,0	—	—	»	—	—	—	—	—	—	—	—	—	—
YbN	314,01	75,0	—	—	»	—	—	—	—	—	—	—	—	—	—
LuN	314,01	75,0	—	—	»	—	—	—	—	—	—	—	—	—	—
Th_3N_4	1297,91	310,0	178,78	42,7	»	2373	—	—	116,309	27,78	133,14	31,8	—	—	298—800
UN	286,80	68,5	75,36	18,0	»	2903	—	—	44,38	10,6	29,31	7,0	—	—	298—3000
U_2N_3	891,79	213,0	121,42	29,0	»	—	—	—	—	—	—	—	—	—	—
PuN	32,66	7,8	—	—	»	—	—	—	—	—	—	—	—	—	—
TiN	336,62	80,4	30,31	—	»	—	—	—	—	—	—	—	—	—	—
$ZrN_{0,58}$	218,97	52,3	39,36	9,4	»	—	—	—	—	—	—	—	—	—	—
Zr_3N_4	22,19	5,3	—	—	»	—	—	—	90,602	21,64	108,857	26,00	—	—	—
$ZrN_{0,69}$	268,37	64,1	40,61	9,7	»	—	—	—	—	—	—	—	—	—	—
$ZrN_{0,74}$	281,77	67,3	40,61	9,7	»	—	—	—	—	—	—	—	—	—	—
$ZrN_{0,80}$	319,45	76,3	38,93	9,3	»	—	—	—	—	—	—	—	—	—	—
ZrN	365,51	87,3	38,93	9,3	»	3223	—	—	46,473	11,10	7,031	1,68	—7,29[illegible]	—1,75	298—1700
HfN	369,44	88,24	54,85	13,1	»	3255	—	—	41,20	9,84	9,29	2,22	—	—	298—3000
VN	251,21	60,0	37,26	8,9	»	2323	—	—	45,804	10,94	8,79	2,1	—9,253	—2,21	298—1300
NbN	255	61,1	—	—	»	—	—	—	—	—	—	—	—	—	—

Designation: npesp = transition.

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Table 18 (Cont'd).

Compound	ΔH°_{298} kJ/mole	ΔH°_{298} kcal/mole	S°_{298} J/mole·deg	S°_{298} cal/mole·deg	Phase	T_{transp}, °K	$-\Delta H_{transp}$ kJ/mole	$-\Delta H_{transp}$ kcal/mole	Heat capacity $C_p = a + bT + cT^{-2}$: a J/mole·deg	a cal/mole × deg	b·10³ J/mole·deg	b·10³ cal/mole × deg	c·10⁻⁵ J/mole·deg	c·10⁻⁵ cal/mole × deg	Temperature interval, °K
NbN	237.81	56.8	43.96	10.5	Solid	2323	—	—	48,283	8.89	22,609	5.40	—	—	298—800
Ta_2N	270.89	64.7	—	—	»	—	—	—	—	—	—	—	—	—	—
TaN	247.02	59.0	51.08	12.2	»	3363	—	—	52,364	7.73	32,657	7.80	—	—	298—800
Cr_2N	105.51	25.2	75.36	18.0	»	—	—	—	39,84	15,34	28,47	6,8	—	—	273—800
CrN	118.07	28.2	35.49	8.0	»	Decomposes	—	—	41,38	9,84	16,33	3,9	—	—	273—800
Mo_2N	69.50	16.6	57.92	21.0	»	—	—	—	46,86	11,19	57,778	13,80	—	—	298—800
W_2N	72.01	17.2	—	—	»	—	—	—	—	—	—	—	—	—	—
Mn_4N	130.63	31.2	—	—	»	—	—	—	92,779	22,16	127,78	30,5	—	—	298—800
$Mn_{2.5}N$	115.56	27.6	—	—	Solid	—	—	—	—	—	—	—	—	—	—
Mn_3N_2	201.80	48.2	192.17	45.9	»	—	—	—	127,987	30,55	160,773	38,40	—	—	298—800
Mn_6N_2	—	—	—	—	»	—	—	—	94,203	22,5	94,20	22,5	—	—	298—800
Re_4N	—4.19	—1.0	—	—	»	—	—	—	—	—	—	—	—	—	—
Fe_8N	11.30	2.7	—	—	»	—	—	—	—	—	—	—	—	—	—
Fe_4N	10.89	2.6	156.17	37.3	»	943	—	—	112,37	26,84	34,16	8,16	—	—	273—1000
Fe_2N	3.77	0.9	101.32	24.2	»	—	—	—	62,43	14,91	25,50	6,09	—	—	273—1000
Co_3N	—8.37	—2.0	—	—	»	Decomposes	—	—	—	—	—	—	—	—	—
Ni_3N	—0.84	—0.2	—	—	»	»	—	—	—	—	—	—	—	—	—
BN	254.14	60.7	15.37	3.67	»	3273	—	—	7,62	1,82	15,16	3,62	—	—	298—1200
	—	—	—	—	Liquid	5340	—	—	—	—	—	—	—	—	—
	—379.32	—90.6	86.96	20.77	Gaseous	—	—	—	30,14	7,20	4,44	1,06	—1,76	—0,42	298—2500
AlN	320.29	76.5	20.93	5.0	Solid	Decomposes	—	—	22,90	5,47	32,66	7,80	—	—	293—900
GaN	104.67	25.0	46.47	11.1	»	»	—	—	—	—	—	—	—	—	—
InN	19.26	4.6	42.71	10.2	»	»	—	—	—	—	—	—	—	—	—
Si_3N_4	749.44	179.0	96.30	23.0	»	2173	—	—	70,464	16,83	98,81	23,6	—	—	298—900
Ge_3N_4	65.31	15.6	167.47	40.0	»	Decomposes	—	—	—	—	—	—	—	—	—
PN	—84.57	—20.2	211.18	50.44	Gaseous	—	—	—	31,150	7,44	3,768	0,90	—2,303	—0,55	298—2000
$\frac{1}{n}(PN)_n$	70.34	16.8	—	—	Solid	—	—	—	—	—	—	—	—	—	—
P_3N_5	316.94	—	—	—	»	—	—	—	149,05	35,6	—	—	—	—	298
AsN	—29.31	—7.0	—	—	Gaseous	—	—	—	33,66	8,04	2,26	0,54	—3,48	—0,83	298—2000
SbN	—312.75	—74.4	—	—	»	—	—	—	34,583	8,26	1,758	0,42	—3,601	—0,86	298—2000

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Table 19. Thermodynamic potentials of nitride formation.

Reaction	$-\Delta Z°_{298}$		$\Delta Z_T = a + bT \lg T + cT$						Temperature interval, °K
			a		$b \cdot 10^3$		$c \cdot 10^6$		
	kJ/mole	kcal/mole	kJ/mole	kcal/mole	kJ/mole	kcal/mole	kJ/mole	kcal/mole	
$3Li_{(тв)} + {}^1/_2N_{2(г)} = Li_3N_{(тв)}$	—	—	198,75	—47,47	—	—	142,35	34,0	—
$3Be_{(тв)} + N_{2(г)} = Be_3N_{2(тв)}$	513,306	122,601	—563,962	—134,7	—	—	169,984	40,6	298—1000
$3Mg_{(тв)} + N_{2(г)} = Mg_3N_{2(тв)_\alpha}$	399,722	95,472	—458,873	—109,6	—	—	198,496	47 41	298—923
$3Mg_{(ж)} + N_{2(г)} = Mg_3N_{2(тв)_\beta}$	—	—	—485,25	—115,97	—	—	227,343	54,3	923—1061
$3Mg_{(ж)} + N_{2(г)} = Mg_3N_{2(тв)_\gamma}$	—	—	484,622	—115,75	—	—	226,464	54,09	1061—1300
$3Ca_{(тв)} + N_{2(г)} = Ca_3N_{2(тв)}$	377,231	90,1	—439,614	—105,0	—	—	209,34	50,0	298—1000
$3Sr_{(тв)} + N_{2(г)} = Sr_3N_{2(тв)}$	—	—	—382,67	—91,4	—	—	213,11	50,9	—
$3Ba_{(тв)} + N_{2(г)} = Ba_3N_{2(тв)}$	292,636	69,895	—364,252	—87,0	—	—	240,322	57,4	298—1000
$La_{(тв)} + {}^1/_2N_{2(г)} = LaN_{(тв)}$	270,677	64,65	—301,868	—72,1	—	—	104,67	25,0	298—1000
$Ce_{(тв)} + {}^1/_2N_{2(г)} = CeN_{(тв)}$	295,379	70,55	—328,57	—78,6	—	—	104,67	25,0	298—1000
$3Th_{(тв)} + 2N_{2(г)} = Th_3N_{4(тв)}$	1187,665	283,669	—1299,583	—310,4	—	—	375,556	89,7	298—2000
$U_{(тв)} + {}^1/_2N_{2(г)} = UN_{(тв)}$	259,971	62,093	—288,796	—68,5	—	—	90,016	21,5	298—2000
$3U_{(тв)} + 2N_{2(г)} = U_3N_{4(тв)}$	—	—	1151,4	—275,0	—	—	342,9	81,9	—
$Ti_{(тв)_\alpha} + {}^1/_2N_{2(г)} = TiN_{(тв)}$	308,291	73,634	—335,991	—80,25	—	—	92,947	22,2	298—1155
$Ti_{(тв)_\beta} + {}^1/_2N_{2(г)} = TiN_{(тв)}$	—	—	—338,503	—80,85	—	—	95,375	22,78	1155—1500
$Zr_{(тв)_\alpha} + {}^1/_2N_{2(г)} = ZrN_{(тв)}$	336,422	80,353	—364,252	—87,0	—	—	93,387	22,306	298—1135
$Zr_{(тв)_\beta} + {}^1/_2N_{2(г)} = ZrN_{(тв)}$	—	—	—	—	—	—	—	—	—
$Hf_{(тв)} + {}^1/_2N_{2(г)} = HfN_{(тв)}$	340,806	81,4	—340,806	—81,4	—	—	—	—	298
$V_{(тв)} + {}^1/_2N_{2(г)} = VN_{(тв)}$	223,797	53,453	—[illegible]	—[illegible]	—7,327	—1,75	110,115	26,3	298—2000
$Ta_{(тв)} + {}^1/_2N_{2(г)} = TaN_{(тв)}$	218,183	52,112	—246,603	—58,9	—28,889	—6,9	166,844	39,85	298—2240
$2Cr_{(тв)} + {}^1/_2N_{2(г)} = Cr_2N_{(тв)}$	85,227	20,356	—108,647	—25,95	—24,074	—5,75	138,164	33,0	298—1400
$Cr_{(тв)} + {}^1/_2N_{2(г)} = CrN_{(тв)}$	94,287	22,52	—127,28	—30,4	—19,26	—4,6	158,39	37,83	298—1300
${}^1/_2Cr_2N_{(тв)} + {}^1/_2N_{2(г)} = CrN_{(тв)}$	49,915	11,922	—66,989	—16,0	—12,037	—2,875	87,085	20,8	298—1400
$2Mo_{(тв)} + {}^1/_2N_{2(г)} = Mo_2N_{(тв)}$	50,095	11,965	—72,3.3	—17,2	—19,259	—4,6	121,208	28,95	298—1500

Table 19 (Cont'd).

Reaction	$-\Delta Z°_{298}$		$\Delta Z_T = a + bT\ln T + cT$						Temperature interval, °K
			a		$b \cdot 10^3$		$c \cdot 10^6$		
	kJ/mole	kcal/mole	kJ/mole	kcal/mole	kJ/mole	kcal/mole	kJ/mole	kcal/mole	
$5Mn_{(тв)} + N_{2(г)} = Mn_5N_{2(г)}$	—	—	—69,501 —241,87	—16,6 —57,77	—	—	87,923 152,4	21,0 36,4	1500—2000 —
$3Mn_{(ж)} + N_{2(г)} = Mn_3N_{2(тв)}$	—	—	—191,76	—45,8	—	—	149,47	35,7	—
$4Fe_{(тв)} + {}^1/_2N_{2(г)} = Fe_4N_{(тв)}$	—4,032	—0,963	—0,837	—0,2	48,661	11,62	-104,042	—24,85	298—950
$Al_{(тв)} + {}^1/_2N_{2(г)} = AlN_{(тв)}$	294,621	70,369	—322,384	—77,0	—	—	93,156	22,25	298—923
$Al_{(ж)} + {}^1/_2N_{2(г)} = AlN_{(тв)}$	—	—	—265,862	—63,5	—	—	115,137	27,5	1800—2000
$B_{(тв)} + {}^1/_2N_{2(г)} = BN_{(тв)}$	—	—	—108,857	—26,0	—	—	40,612	9,7	1200—2300
$B_{(ж)} + {}^1/_2N_{2(г)} = BN_{(тв)}$	—	—	—656,909	—156,9	—	—	223,994	53,5	2500—3000
$3Si_{(тв)} + 2N_{2(г)} = Si_3N_{4(тв)}$	653,312	156,041	—753,624	—180,0	—	—	836,819	80,4	298—1680
$3Si_{(ж)} + 2N_{2(г)} = Si_3N_{4(тв)}$	—	—	—883,463 —790,468	—213,4 —188,8	—	—	419,517 412,4	100,2 98,5	1680—1800 1800—2000

Calculating the heat capacity of certain nitrides. In the process of oxidation of refractory compounds analogous to that, observed in the oxidation of metals and alloys, a multilayer cinder will be formed, consisting of several oxide phases, among which at high temperatures the occurrence of various exchange reactions is possible, considerably varying the composition of the cinder and the condition of the diffusion through it the reaction components.

The explanation of the thermodynamic stability of refractory compounds in different media and the determination of the thermodynamic possibility of the occurrence of oxidation-reduction reactions in a layer of the cinder consists in determining the isobaric-isothermic potentials [Gibbs free energies] of corresponding reactions at different temperatures.

These values can be calculated by several methods, of which the one deserving the greatest attention is the method of determining

thermodynamic values, in which the values of heat capacities C_p at various temperatures, the heats of formation ΔH^0_{298} and absolute entropy S^0_{298} the reaction components in the standard state are used [863], and also a method, at the basis of which lies the use of the given thermodymamic potentials [864].

The values of the latter for many compounds and elements in the gaseous and condensed states are given in special tables [864]. The latter method is extraordinarily simple since consists in the direct calculation of the isobaric-isothermic potential [Gibbs free energy] ΔZ^0_T of reactions according to certain data of the heats of formation and given thermodynamic potentials of the reaction components.

However up to now the values of the given thermodynamic potentials exist only for a few nitrides and carbides which excludes the possibility of the use of this method for the broad class of compounds. Therefore the calculation ΔZ^0_T of reactions with the participation of borides and silicide, and also the greater part of the carbides, nitrides and sulfides is possible only by the first method which certain equations of the temperature dependence of heat capacity.

For the greater number of refractory compounds in literature the corresponding values of the power series of heat capacity are absent. Therefore the values of the heat capacities of nitrides of the simplest type were calculated (Table 20), using the Debye method [863].

The values of the heat capacities of nitrides at a constant volume (C_V) were determined by interpolation of the table values of the Debye functions $3C_D$ for values of the calculated values Θ'/T at all temperatures taken for calculation.

The characteristic temperature of an element was determined by the Lindemann formula

$$\theta = 135\sqrt{\frac{T_{пл}}{M \cdot V^{2/3}}}.$$

where $T_{пл}$ is the melting point of the element, M is the atomic weight, V is the atomic volume.

Table 20. Characteristic temperatures of certain elements and compounds.

Substance	$T_{пл}$, °K	V, cm	Characteristic temperature, °K		
			θ	θ'	
				for a metal in corresponding compound	for a metal in corresponding compound
Sc	1673	14,99	44	—	—
Hf	2273	13,62	202	—	—
Th	1973	21,18	144	—	—
U	1408	12,49	141	—	—
N_2	63	17,3	587	—	—
ScN	2923	—	—	578	754
HfN	3255	—	—	241	796
ThN	2903	—	—	175	752
UN	2923	—	—	204	754

According to the theoretical concepts, developed in [863, 865], the characteristic temperature θ' for an element in a compound was calculated by the formula

$$\theta' = \theta\sqrt{\frac{T'_{пл}}{T_{пл}}},$$

where θ is the characteristic temperature of the free element, $T'_{пл}$ and $T_{пл}$ are respectively the absolute melting point of the compound and the element.

The values of the melting points $T_{пл}$ and the molar (atomic) volumes V of metals, nitrogen and nitrides, and also the values of the calculated characteristic temperatures are represented in Table 20.

Using value θ' and summarizing the values of the atomic heat capacities found according to the curve $3C_D = f(\theta/T)$, the heat capacity C_V of refractory compounds at a given temperature was determined. The transition to values of heat capacities at constant pressure was accomplished with the help of approximate formula

$$C_p = C_V\left(1 + 0{,}0214\, C_V \frac{T}{T_{пл}}\right).$$

The experimental values C_p for titanium carbide were compared with the values, calculated by the above described method. The coincidence of theoretical and experimental values of C_p was satisfactory (Fig. 24). In the region of high temperatures, higher than 673°C, the complete correspondence of calculated and experimental data was observed; maximum divergence observed in region of temperatures 273-473°K was about 5% of C_p.

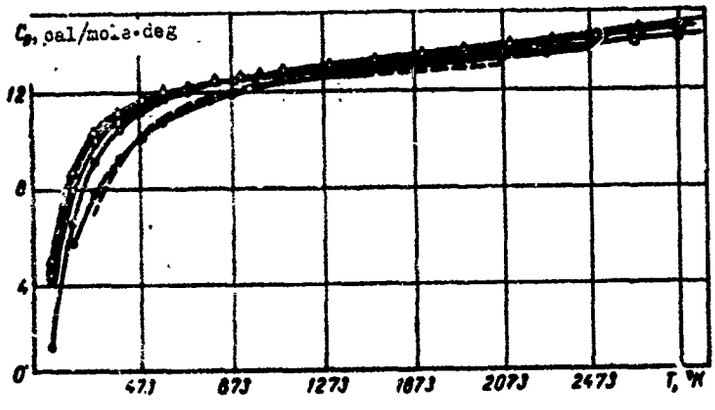


Fig. 24. The temperature dependence of the heat capacity of certain nitrides: □—HfN; ○—ScN; ▲—ThN; ×—UN; ●—TiC (calculated); ---TiC (experimental).

The calculated values of heat capacities C_p for the nitrides enumerated in Table 20 at different temperatures are given in Table 21, and on Fig. 24 this dependence for nitrides is graphically shown. The temperature dependence of these values can be represented by equation

$$C_p = a + bT \cdot 10^{-3} T - c \cdot 10^{5} \cdot T^{-2}.$$

Table 21. The values of heat capacity C_p of nitrides at different temperatures, $cal \cdot deg^{-1} \cdot mole^{-1}$.

Temperature °K	ScN	HfN	ThN	UN
73	1,21	4,00	4,93	4,57
173	6,49	7,97	8,64	8,34
273	9,10	9,95	10,22	10,18
373	10,46	10,88	11,10	11,03
473	11,18	11,46	11,62	11,57
573	11,64	11,78	11,92	11,89
673	11,97	12,07	12,19	12,16
773	12,32	12,28	12,39	12,36
873	12,42	12,43	12,56	12,53
973	12,59	12,58	12,71	12,68
1073	12,78	12,71	12,85	12,84
1173	—	—	12,99	13,01
1273	13,03	12,95	13,11	13,10
1473	13,28	13,17	13,35	13,33
1673	13,53	13,38	13,58	13,57
1873	13,76	13,59	13,81	13,79
2073	13,98	13,78	14,02	14,01
2273	14,19	—	14,24	14,23
2473	14,42	14,17	14,46	14,44
2673	14,64	—	14,67	14,66
2873	14,85	14,56	14,39	14,86
3073	—	—	—	15,07

The values of the constants of equations of the temperature dependence of the heat capacity of nitrides are represented in Table 22.

Table 22. Values of constants a, b, c of the equation $c_p = a + b \cdot 10^{-3} T - c \cdot 10^5 T^{-2}$.

Connections	a	$b \cdot 10^3$	$c \cdot 10^5$
ScN	11,59	1,23	2,06
HfN	11,68	1,07	1,48
ThN	11,66	1,19	1,31
UN	11,62	1,23	1,39

Thus, in the absence of experimental data on heat capacity the Debye method can be successfully used for evaluating the heat capacity of nitrides of the simplest type.

Having the necessary thermodynamic values available, it is possible to carry out the thermochemical calculation of the interaction in a nitride-gaseous phase system, thereby determining the stability of refractory compounds in different media.

Calculating given thermodynamic potentials of certain nitrides. The simple and convenient method of considering thermodynamic equilibriums in a refractory compound-gaseous phase system and estimating the isobaric-isothermic potentials [Gibbs free energies] of the reactions of the interaction of the components of such systems consist in the direct calculation of the isobaric-isothermic potentials [Gibbs free energies] of the reaction, in using the data of the heats of formation in the standard state ΔH^0_{298} and the given thermodynamic potentials of the reaction components. The values of the latter for elements and many compounds in the condensed and gaseous states are given in special tables [864]. However values of given thermodynamic potentials exist only for certain carbides and nitrides and the values of these magnitudes for borides and silicide are completely lacking.

As is known, the given thermodynamic potential (Table 23) of Φ^*_T will be formed by adding the enthalpy function $H^0_T - H^0_{T_1}/T$ to both sides of the equation:

$$\frac{Z_T - H^0_1}{T} = -S^0_T \qquad \text{(I.3)}$$

obtaining

$$\Phi^*_T = \frac{Z^0_T - H^0_1}{T} = -S^0_T + \frac{H^0_T - H^0_1}{T}, \qquad \text{(I.4)}$$

where index ^{0} designates the standard state; T is the temperature, °K, and for temperature T_1 there is usually assumed 298.15°K. For the condensed phases Φ_T^* there can be obtained from

$$\Phi_T^* = \int_{T_1}^{T} (H_T^0 - H_{T_1}^0) d\left(\frac{1}{T}\right) - S_T^0 \qquad (I.5)$$

or, using the value of heat capacity,

$$\Phi_T^* = \frac{1}{T}\int_{T_1}^{T} C_p^0 dT - \int_0^T \frac{C_p^0 dT}{T}. \qquad (I.6)$$

Table 23. Values of the given thermodynamic potentials $\Phi_T^* = \frac{\Phi_T^0 - H_{298}^0}{T}$ of certain nitrides at various temperatures, cal·deg^{-1} × × mole^{-1}.

Nitride	298°K	500°K	1000°K	1500°K	2000°K
Li_3N	32,9	79,8	—	—	—
Be_3N_2	12,0	20,3	23,2	33,7	44,4
Mg_3N_2	19,5	23,1	34,6	43,5	—
Ca_3N_2	25,6	28,6	40,2	—	—
Ba_3N_2	34,2	38,1	49,5	—	—
LaN	13,6	13,9	17,4	—	—
CeN	16,0	17,2	21,4	—	—
Th_3N_4	43,2	45,8	59,5	71,7	82,5
UN	13,4	14,6	19,2	23,8	27,7
TiN	6,5	8,2	12,7	16,2	—
ZrN	8,8	10,4	14,7	18,2	—
HfN	10,85	—	—	—	—
VN	8,9	10,1	14,4	18,0	—
NbN	10,7	11,7	16,3	20,2	23,5
TaN	6,4	10,5	17,6	22,3	25,8
Cr_2N	18,0	20,0	27,4	34,9	—
CrN	5,2	6,0	7,3	7,8	—
Mo_2N	21,0	22,9	29,9	35,7	32,8
Mn_3N_2	47,6	52,5	—	—	—
Mn_4N_3	33,0	36,3	—	—	—
Fe_2N	24,5	26,4	33,3	—	—
Fe_4N	36,9	40,8	52,6	—	—
AlN	9,2	9,5	13,2	—	8,0

For the standard temperature there is usually assumed 298.15°K. The connection between the two standard temperatures is carried out by using H^0_{298} in the following way:

$$\frac{Z^0_T - H^0_{298}}{T} + \frac{H^0_{298} - H^0_0}{T} = \frac{Z^0_T - H^0_0}{T}. \qquad (I.7)$$

For the chemical reaction $\Delta\Phi^*_T$ is determined in this way, as well as ΔH or ΔZ.

$$\Delta\Phi^\circ_T = \Sigma\Phi^\circ_T \text{ the reaction of products} - \Sigma\Phi^\circ_T \text{ of the initial components} \qquad (I.8)$$

Since

$$\Delta\Phi^\circ_T = \frac{\Delta Z^0_T}{T} - \frac{\Delta H^0_T}{T} \qquad (I.9)$$

and

$$\Delta Z^0_T = -RT\ln K. \qquad (I.10)$$

then

$$-R\ln K = \frac{\Delta H^0_T}{T} + \Delta\Phi^\circ_T \qquad (I.11)$$

and

$$\Phi^\circ_T \text{ of the compound} = \frac{\Delta Z^0_T}{T} - \frac{\Delta H^0_T}{T} + \Sigma\Phi^\circ_T \text{ of the initial components} \qquad (I.12)$$

Thus, using the relationships (I.12), it is possible to determine the value of the given thermodynamic potential of a refractory compound, if the values of the isobaric-isothermic potentials [Gibbs free energies] $\Delta\Phi^0_T$ of the formation reaction of the compound at different temperatures and the values of its heats of formation ΔH^0_{298} in the standard state are known.

The values $\Delta\Phi^0_T$ of the formation reaction of nitrides (Table 23) were determined from equations of the temperature dependence of their isobaric-isothermic potentials [Gibbs free energies], given in [862]. The values of the given thermodynamic potnetials of the corresponding metals and nitrogen were taken from [864].

Having the necessary data ΔZ^0_T and ΔH^0_{298} of the connections available, and also the values of the given thermodynamic potentials of the corresponding metals and nitrogen, the values Φ^*_T of the nitrides were calculated in accordance with equation (I.12).

The knowledge of the given thermodynamic potentials of certain nitrides makes it possible to considerably simplify the calculations of the thermodynamic potentials of the reactions, occurring with the participation of these compounds, not resorting to the laborious method of determining these values, using the thermodynamic relationships (I.3) with respect to the known values of the heats of formation ΔH^0_{298} and of the absolute entropies S^0_{298}, and also the heat capacity c_p of the reaction components in a broad region of temperatures.

The thermodynamic stability of nitrides in different media. The stability of refractory compounds is an important factor, determining their successful use as high-temperature materials.

Higher stability is indicated by a large positive value of standard free energy of the interaction reaction of a refractory connection with a given gaseous phase. However, a certain interaction is observed even at positive value ΔZ^0_T thanks to the fact that the

reaction products can exist with activities, less than unity, for example, in their dissolution in the initial components. At a large positive value of ΔZ^0_T reaction becomes practically impossible.

It is also necessary to consider the kinetics of the reactions. In certain cases interaction with the surroundings is so weak that the use of the material under given conditions is possible, although from the thermodynamic point of view it is unstable. Thus, thermodynamics, being a reliable means of predicting potentially stable compounds under given conditions, does not make it possible to obtain a comprehensive evaluation of the stability of compounds. Let us consider certain regularities of the thermodynamic stability of nitrides in a medium of air, carbon and in a vacuum.

a. <u>The stability of nitrides in an air medium</u>. Below the thermodynamic conditions of the course of the interaction reaction of nitrides with air at a pressure, equal to 1 at (0.2 at O_2 and 0.8 at N_2) are examined, and the results of the thermodynamic calculation of equilibriums in nitride-oxygen system and the determination of the pressure equilibrium of the gaseous products of the interaction reaction of a number of nitrides TiN, ZrN, VN, BN, Si_3N_4 with the oxygen of the air are given.

To calculate the thermodynamic values the given thermodynamic potentials, tabulated for elements and compounds in gaseous and condensed states in the special tables [864], were used. The calculation is presented in accordance with equation (I.11).

For reactions, proceeding with the production of gaseous products, equilibrium constant K can be represented as

$$K_p = \frac{p}{p_{O_2}}, \qquad (I.13)$$

where p is the partial pressure of the gaseous product of the reaction, p_{O_2} is the partial pressure of atmospheric oxygen at atmospheric

pressure p_i = 1 at. Equation (I.11) takes the form

$$-R\ln K = \frac{p}{p_0} - \frac{\Delta H^0_{298}}{T} + \Delta\Phi^*_T \qquad (I.14)$$

Inasmuch as p_{O_2} of the air is 0.2 at (p_{N_2} = 0.8 at), the problem reduces to determination of the pressure of the gaseous products of the reaction p_{N_2}(NO) from certain tabular values ΔH^0_{298} and Φ^*_T of the reaction components.

The possible interaction reactions of the nitrides TiN, ZrN, VN, BN and Si_3N_4 with the oxygen of the air (0.2 at) are presented in Table 24, from which it is evident that the interaction of nitrides with oxygen can occur both with the formation of nitrogen, and also of its oxide NO.

Table 24. The equilibrium pressure N_2 or NO of the oxidation reactions of certain nitrides $\lg p = -\frac{A}{T} + B$.

Reaction	$-A$	$B \cdot 10^{-3}$
$2ZrN + 2O_2 = 2ZrO_2 + N_2$	5.0	79
$2TiN + 2O_2 = 2TiO_2 + N_2$	11.5	83
$2TiN + {}^3/_2O_2 = Ti_2O_3 + N_2$	7.5	54
$2TiN + {}^5/_2O_2 = Ti_2O_5 + N_2$	6.5	48
$2TiN + O_2 = 2TiO + N_2$	1.0	22
$2ZrN + {}^5/_2O_2 = Zr_2O_5 + N_2$	5.0	32
$TiN + O_2 = TiO + NO$	1.5	26
$TiN + {}^3/_2O_2 = TiO_2 + NO$	3.0	30
$TiN + {}^5/_4O_2 = {}^1/_2Ti_2O_5 + NO$	2.0	22
$TiN + {}^3/_4O_2 = {}^1/_2Ti_2O_3 + NO$	0.0	7
$2VN + {}^5/_2O_2 = V_2O_5 + N_2$	14.5	84
$2VN + 2O_2 = V_2O_4 + N_2$	8.5	58
$2VN + {}^3/_2O_2 = V_2O_3 + N_2$	1.0	26
$Si_3N_4 + {}^3/_2O_2 = {}^3/_2SiO_2 + N_2$	5.5	5
$2BN + {}^3/_2O_2 = B_2O_3 + N_2$	5.0	38.5
$2VN + O_2 = 2VO + N_2$	5.2	41
$Si_3N_4 + {}^3/_2O_2 = {}^3/_2SiO_2 + NO$	5.0	43.3
$VN + {}^3/_4O_2 = {}^1/_2V_2O_3 + NO$	6.1	27
$VN + {}^5/_4O_2 = {}^1/_2V_2O_5 + NO$	5.0	24.5
$VN + {}^7/_4O_2 = {}^1/_2V_2O_7 + NO$	2.7	20.5
$VN + O_2 = VO + NO$	5.0	8

The calculated values of the equilibrium pressures of the gaseous products of reaction in accordance with equation (I.12) at different temperatures (from 298 to 2000°K) are represented in Table 24 by equations of the temperature dependence of the pressures of N_2 and NO.

Nitrides are characterized by higher thermodynamic stability (large negative values ΔZ^0_T), than the corresponding carbides at low temperatures, but by considerably less free energy of the formation of the corresponding oxides. Therefore nitrides rapidly decompose upon heating in air (or in oxygen) with the formation of stabler connections-oxides. Considering that the thermodynamic stability of nitrides, oxides and nitrogen decreases with temperature increase, the value of the free energy of an interaction reaction of nitride with oxygen also decreases with the increase in temperature.

From a consideration of curves log p = f(T) (Figs. 25, 26) it follows that the variation in the free energy of reaction and the pressure of nitrogen and nitrogen oxide decreases with the increase in temperature, i.e., thermodynamic stability of nitrides in air is increased. At certain definite temperatures for a given oxidation reaction of a nitride $\Delta Z^0_T = 0$, i.e., the occurrence of the process becomes thermodynamically improbable. An evaluation of the values of these temperatures shows that they lie in a region of very high values (more than 6000°K), exceeding by far the usual temperature regions of experimental investigations. Consequently, at normal temperatures the oxidation process of nitrides is characterized by high thermodynamic probability and occurs spontaneously in the direction of the formation of more stable reaction products.

The calculated pressures of gaseous N_2 and NO do not consider the protective nature of the cinder layer forming. Nevertheless under conditions of constant gas generation the forming layer of oxides is gradually disintegrated and the observed pressure of N_2 and NO can sometimes be very close to the calculated values.

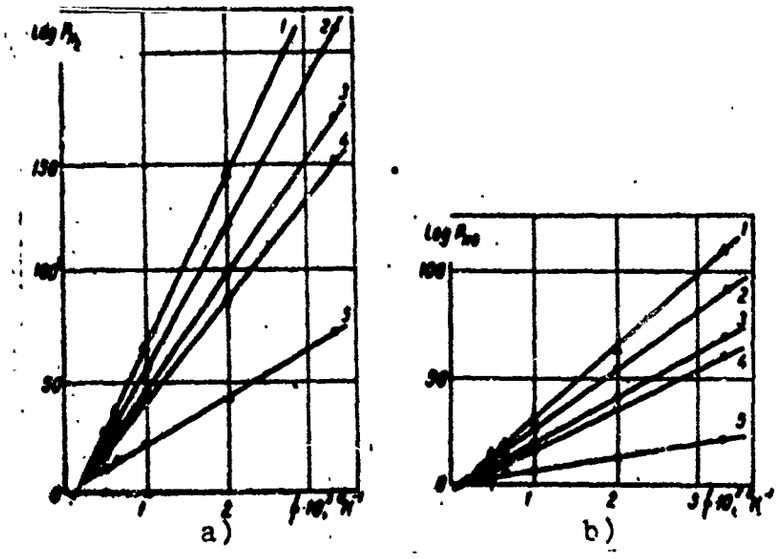


Fig. 25. The temperature dependence of isobaric-isothermic potentials [Gibbs free energies] of the oxidation reactions of TiN and ZrN:

a) 1 — $2ZrN+2O_2=2ZrO_2+N_2$; 2 — $2TiN+2O_2=2TiO_2+N_2$; 3 — $2TiN+{}^3/_2O_2={}^1/_2Ti_2O_3+N_2$; 4 — $2TiN+{}^1/_2O_2=Ti_2O_3+N_2$; 5 — $2TiN+O_2=2TiO+N_2$;

b) 1 — $ZrN+O_2=ZrO_2+NO$; 2 — $TiN+O_2=TiO+NO$; 3 — $TiN+{}^3/_2O_2=TiO_2+NO$; 4 — $TiN+{}^1/_2O_2={}^1/_2Ti_2O_3+NO$; 5 — $TiN+{}^5/_4O_2={}^1/_2Ti_2O_5+NO$.

As can be seen from Figs. 25, 26 the thermodynamic possibility of the occurrence of the oxidation reaction nitrides with the production of the corresponding oxide and gaseous nitrogen is much greater than the thermodynamic possibility of the oxidation reactions, the product of which is NO. Actually, nitrogen oxide is characterized in contrast to other compounds by a comparatively large negative thermal effect of formation and by high value of entropy. This determines the lower value of the free energy of the reactions, the product of which is NO.

For a given nitride, the oxidation products of which can be several different oxides, the thermodynamic possibility is maximum for reactions, proceeding with the formation of the highest oxides of the given metal. In oxygen medium, in spite of the fact that $\Delta Z^0_{ZrN} > \Delta Z^0_{TiN}$, titanium nitride is thermodynamically stabler than

zirconium nitride, thanks to the lower value of the free energy of the formation of TiO_2 as compared to ZrO_2.

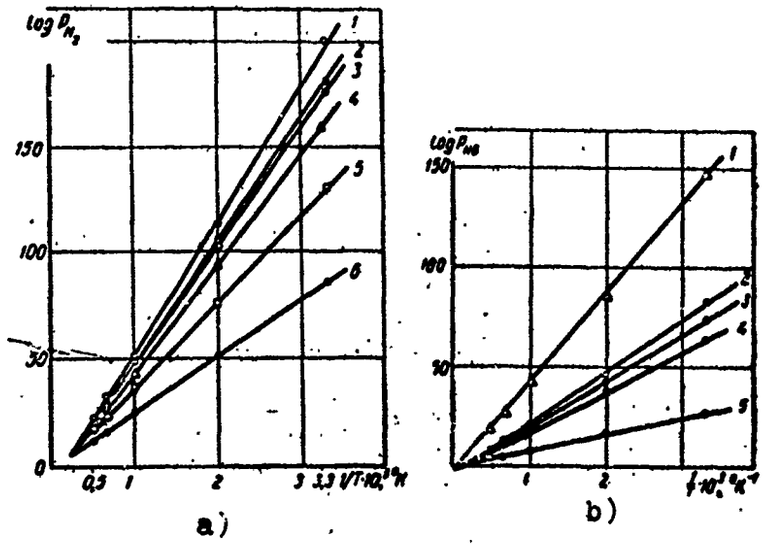


Fig. 26. The temperature dependence of isobaric-isothermic potentials [Gibbs free energies] of the oxidation reactions of VN, BN and Si_3N_4:

a) 1—$2VN + {}^5/_2O_2 = V_2O_5 + N_2$; 2—$2VN + 2O_2 = V_2O_5 + N_2$; 3—$2VN + {}^5/_2O_2 = V_2O_5 +$
b) $+ N_2$; 4—$Si_3N_4 + 3O_2 = 3SiO_2 + 2N_2$; 5—$2BN + {}^5/_2O_2 = B_2O_3 + N_2$; 6—$2VN + O_2 = 2VO + N_2$.
1—$Si_3N_4 + 5O_2 = 3SiO_2 + 4NO$; 2—$VN + {}^7/_4O_2 = {}^1/_2V_2O_5 + NO$; 3—$VN + {}^5/_4O_2 = {}^1/_2$
$V_2O_5 + NO$; 4—$VN + {}^5/_4O_2 = {}^1/_2V_2O_5 + NO$; 5—$VN + O_2 = VO + NO$;

From a consideration of thermodynamic equilibrium in nitride-oxygen systems and the values of the pressure of the gaseous reaction products, it follows that in the temperature interval 298-2000°K the nitrides are unstable in oxygen and can be subjected to oxidation with the formation of the corresponding oxides and gaseous products N_2 and NO.

The interaction reactions of nitrides with oxygen, the products of which is nitrogen, are characterized by higher values of negative free energy than reactions, occurring with the formation of NO. Therefore in analyzing the products of the oxidation reaction of nitrides, as a rule, only nitrogen is detected.

The stability of nitrides in a vacuum. Nitrides are characterized by higher values of free energy of formation than the corresponding carbides and sulfides. The thermodynamic stability of nitrides is

usually higher than the thermodynamic stability of the corresponding carbides at 298°K, however the value of the absolute values of the entropy of the formation of nitrides is higher, which also determines the sharp decrease in the free energy of the formation of nitrides with a temperature rise.

Due to relatively low thermodynamic stability at high temperatures nitrides are characterized by high values of the dissociation of nitrogen, and this factor to a greater degree than the values of their melting points, limits possibility of their use as refractory materials.

In Table 25 the calculated values of the equilibrium pressures of nitrogen during the dissociation of certain nitrides are presented

$$\log p_{N_2} = -\frac{\Delta Z_T^0}{2{,}303 \cdot RT},$$

where p_{N_2} is the equilibrium pressure of the dissociation of nitrogen, ΔZ^0_T is the variation in the free energy of the formation of nitride.

Table 25. The values of the partial pressure of nitrogen with the dissociation of certain nitrides.

Reaction	298° K	500° K	1000° K	1500 °K	2000° K
$2Li_3N \rightleftarrows 6Li + N_2$	$6{,}49 \cdot 10^{-66}$	$5{,}65 \cdot 10^{-37}$	—	—	—
$Be_3N_2 \rightleftarrows 3Be + N_2$	$1{,}24 \cdot 10^{-80}$	$1{,}26 \cdot 10^{-51}$	$2{,}85 \cdot 10^{-21}$	—	—
$Mg_3N_2 \rightleftarrows 3Mg + N_2$	$9{,}95 \cdot 10^{-71}$	$3{,}18 \cdot 10^{-38}$	$3{,}33 \cdot 10^{-14}$	$9{,}06 \cdot 10^{-6}$	—
$Ca_3N_2 \rightleftarrows 3Ca + N_2$	$8{,}45 \cdot 10^{-67}$	$1{,}08 \cdot 10^{-35}$	$9{,}55 \cdot 10^{-13}$	—	—
$Ba_3N_2 \rightleftarrows 3Ba + N_2$	$5{,}55 \cdot 10^{-52}$	$3{,}3 \cdot 10^{-26}$	$3{,}4 \cdot 10^{-7}$	—	—
$2LaN \rightleftarrows 2La + N_2$	$1{,}51 \cdot 10^{-85}$	$7{,}95 \cdot 10^{-53}$	$2{,}59 \cdot 10^{-21}$	—	—
$2CeN \rightleftarrows 2Ce + N_2$	$3{,}39 \cdot 10^{-104}$	$5{,}55 \cdot 10^{-58}$	$6{,}84 \cdot 10^{-24}$	—	—
$^1/_3Th_3N_4 \rightleftarrows {}^3/_3Th + N_2$	$9{,}75 \cdot 10^{-105}$	$9{,}31 \cdot 10^{-60}$	$7{,}67 \cdot 10^{-25}$	$1{,}55 \cdot 10^{-13}$	$6{,}97 \cdot 10^{-8}$
$2UN \rightleftarrows 2U + N_2$	$8{,}53 \cdot 10^{-82}$	$3{,}31 \cdot 10^{-51}$	$2{,}87 \cdot 10^{-21}$	$2{,}74 \cdot 10^{-11}$	$2{,}67 \cdot 10^{-6}$
$2TiN \rightleftarrows 2Ti + N_2$	$1{,}01 \cdot 10^{-108}$	$3{,}58 \cdot 10^{-61}$	$4{,}25 \cdot 10^{-26}$	$2{,}51 \cdot 10^{-14}$	—
$2ZrN \rightleftarrows 2Zr + N_2$	$1{,}41 \cdot 10^{-118}$	$1{,}18 \cdot 10^{-67}$	$5{,}3 \cdot 10^{-29}$	$3{,}03 \cdot 10^{-16}$	—
$2VN \rightleftarrows 2V + N_2$	$4{,}01 \cdot 10^{-79}$	$9{,}62 \cdot 10^{-43}$	$9{,}46 \cdot 10^{-18}$	$3{,}83 \cdot 10^{-9}$	$7{,}21 \cdot 10^{-5}$
$2NbN \rightleftarrows 2Nb + N_2$	$7{,}24 \cdot 10^{-75}$	$3{,}36 \cdot 10^{-41}$	$1{,}06 \cdot 10^{-16}$	$9{,}06 \cdot 10^{-9}$	$4{,}94 \cdot 10^{-5}$
$2TaN \rightleftarrows 2Ta + N_2$	$3{,}72 \cdot 10^{-77}$	$6{,}18 \cdot 10^{-43}$	$4{,}23 \cdot 10^{-18}$	$4{,}75 \cdot 10^{-10}$	$3{,}9 \cdot 10^{-6}$
$2Cr_2N \rightleftarrows 4Cr + N_2$	$1{,}4 \cdot 10^{-30}$	$9{,}06 \cdot 10^{-16}$	$3{,}48 \cdot 10^{-5}$	$1{,}96 \cdot 10^{-2}$	—
$2CrN \rightleftarrows 2Cr + N_2$	$9{,}34 \cdot 10^{-34}$	$3{,}42 \cdot 10^{-16}$	$1{,}64 \cdot 10^{-3}$	1,95·10	—
$4CrN \rightleftarrows 2Cr_2N + N_2$	$2{,}03 \cdot 10^{-36}$	$2{,}68 \cdot 10^{-17}$	$4{,}53 \cdot 10^{-4}$	7,02	—
$2Mo_2N \rightleftarrows 4Mo + N_2$	$2{,}83 \cdot 10^{-18}$	$1{,}55 \cdot 10^{-8}$	$1{,}27 \cdot 10^{-1}$	1,8·10	$3{,}55 \cdot 10^{0}$
$Mn_5N_2 \rightleftarrows 5Mn + N_2$	$4{,}07 \cdot 10^{-38}$	$6{,}31 \cdot 10^{-14}$	—	—	—
$Mn_3N_2 \rightleftarrows 3Mn + N_2$	$1{,}67 \cdot 10^{-36}$	$4{,}97 \cdot 10^{-13}$	—	—	—
$2FeN \rightleftarrows 2Fe + N_2$	$4{,}65 \cdot 10^{8}$	$1{,}42 \cdot 10^{4}$	$4{,}3 \cdot 10^{1}$	—	—
$2Fe_4N \rightleftarrows 8Fe + N_2$	2,58·10	$4{,}69 \cdot 10^{2}$	$1{,}94 \cdot 10^{0}$	—	—
$2AlN \rightleftarrows 2Al + N_2$	$6{,}22 \cdot 10^{-104}$	$2{,}6 \cdot 10^{-58}$	$1{,}17 \cdot 10^{-24}$	—	$1{,}39 \cdot 10^{-2}$
$2BN \rightleftarrows 2B + N_2$	$2{,}4 \cdot 10^{-82}$	$2{,}34 \cdot 10^{-46}$	$7{,}55 \cdot 10^{-20}$	$4{,}6 \cdot 10^{-4}$	$3{,}61 \cdot 10^{-2}$

On Fig. 27 the temperature dependence of the equilibrium pressures of nitrogen are given. Temperature dependence log p - 1/T can be described by an equation of the form log p = a + b/T. In Table 26 values a and b are presented accordingly for all the examined nitrides.

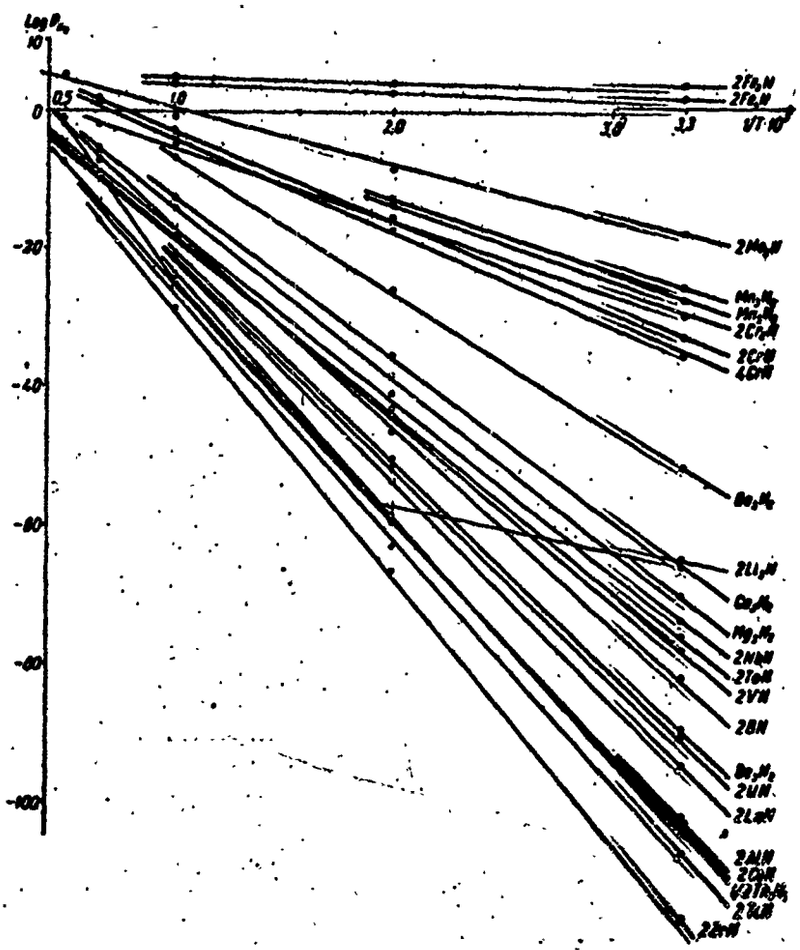


Fig. 27. The temperature dependence of the partial pressures of nitrogen during the dissociation of nitrides.

As follows from Fig. 27, the thermodynamic stability of metal nitrides decreases with an increase in the atomic number of the metal forming the nitride. The highest thermodynamic stability is characteristic for zirconium and titanium mononitrides. They have the lowest

equilibrium pressure of nitrogen and therefore can be used in a vacuum. Somewhat lower stability is possessed by the mononitrides of the rare-earth elements and the actinides, nitrides of group V of the transition metals. The nitrides of group VI are rather unstable. For example, for Mo_2N the partial pressure of nitrogen amounts to 1 at at a temperature of 895°C. Nitrides of group VIII Fe_2N and Fe_4N are characterized by great values of the equilibrium pressure of nitrogen and are thermodynamically unstable in all examined region of temperatures.

The nitrides, the decomposition pressure of which is more than 10^{-6} at, are unstable and highly volatile. From the data of Table 26 it follows that all nitrides, as a rule, are unstable at a temperature of 2000°K.

Table 26. The values of constants a and b of the equation of temperature dependence log p = a + b/T of the partial pressures of nitrogen during the dissociation of certain nitrides.

Compound	a	$b \cdot 10^{-3}$	Compound	a	$b \cdot 10^{-3}$
$2Li_3N$	—43,2	6,8	$2TaN$	7,6	25
Be_3N_2	10	30,4	$2Cr_2N$	5,8	10,4
Mg_3N_2	11	24,4	$2CrN$	10	12,8
Ca_3N_2	12	24	$2Mo_2N$	7,4	10
Ba_3N_2	13,4	19,8	Mn_3N_2	8,4	10,8
$2LaN$	10,6	30,8	Mn_3N_2	8,4	10
$2CeN$	12	35,2	$2Fe_4N$	5	0,4
$^1/_3Th_3N_4$	9,8	34,4	$2Fe_2N$	6	1,2
$2UN$	10,8	30,4	$2AlN$	9,6	34 (298—1000° C)
$2TiN$	9,2	34,9	$2AlN$	20	46 (1000—2000° K)
$2ZrN$	10	38,4	$2BN$	12,8	28,8
$2VN$	9,2	26			
$2NbN$	8	24,4			

In the process of the decomposition of the greater share of the nitrides gaseous nitrogen is liberated and a solid solution of nitrogen in the metal will be formed; other nitirdes, for example UN, form gaseous nitrogen and vapors of the metal.

The values of the partial pressures of nitrogen upon the dissociation of nitrides at a given temperature can also be determined from Fig. 27. To determine the dissociation pressure of a nitride at a given temperature it is necessary to connect point D on extreme left of the vertical line, corresponding to a temperature of absolute zero, with the point on line ΔZ^0_T for the particular nitride and to continue this straight line until it intersects with the right pressure scale. The point of intersection will give the value of the partial pressure of the nitrogen of the nitride at a given temperature.

The stability nitrides in a carbon medium. At high temperatures nitrides are characterized by lower thermodynamic stability than the corresponding carbides, in consequence of which they interact with carbon with the formation of corresponding carbides or carbonitrides and the liberation of gaseous nitrogen.

In spite of the importance of such information, up to now equilibriums in nitride-carbon systems have been little investigated. In work [112] certain thermodynamic data on the interaction reactions of a number of nitrides (AlN, UN, Si_3N_4, TiC) with carbon at a temperature of 2000°K are given.

In Table 27 the results of the thermodynamic calculation of equilibriums in a nitride-carbon system at temperatures of 298, 500, 1000, 1500, 2000°K are presented and the possible assumed reactions between nitrides and carbon (but neglecting the possible formation of carbonitrides).

Let us briefly examine the basic regularities of the processes of the interaction of nitrides with carbon.

The thermodynamic stability of nitrides at 298°C is higher than the thermodynamic stability of the corresponding carbides, however the values of the absolute magnitudes of the entropy of nitrides are higher, which also determines the sharp decrease in the value of the free energy of formation of nitrides with a rise in temperature.

Table 27. Equilibrium pressure of nitrogen of the interaction of a number of nitrides with carbon at different temperatures.

Reaction	Values p_{N_2}, at					Coefficients of the equation		Temperature interval, °K
	298°K	500°K	1000°K	1500°K	2000°K	a	b	
$Mg_3N_2+{}^6/_5C=$ $={}^6/_5Mg_2C_3+N_2$	$1,26\cdot10^{-80}$	$4,90\cdot10^{-50}$	$3,09\cdot10^{-20}$	$1\cdot10^{3}$	—	54	32,2	298—1000
							3,8	1000—1500
$Mg_3N_2+6C=3MgC_2+N_2$	$1,23\cdot10^{-23}$	$1,23\cdot10^{-10}$	2,09	—	—	11	9,72	—
$Ca_3N_2+6C=3CaC_2+N_2$	$5,25\cdot10^{-33}$	$5,25\cdot10^{-14}$	$1,70\cdot10$	—	—	15,25	14,12	—
$^1/_3Th_3N_4+{}^8/_5C=$ $={}^8/_5ThC+N_2$	$1,05\cdot10^{-97}$	$5,37\cdot10^{-56}$	$3,16\cdot10^{-26}$	$1,12\cdot10^{-12}$	$2,29\cdot10^{-7}$	7	32,23	—
$^1/_3Th_3N_4+3C=$ $={}^8/_3ThC_2+N_2$	$4,37\cdot10^{-86}$	$4,27\cdot10^{-30}$	$6,03\cdot10^{-11}$	$1,45\cdot10^{-4}$	$2,46\cdot10^{-1}$	7	19,2	—
$2UN+2C=2UC+N_2$	$1,59\cdot10^{-89}$	$1,05\cdot10^{-31}$	$3,39\cdot10^{-11}$	$1,1\cdot10^{-4}$	$1,99\cdot10^{-1}$	8,2	20,15	—
$2UN+3C=U_2C_3+N_2$	$7,59\cdot10^{-56}$	$9,33\cdot10^{-29}$	$1,59\cdot10^{-10}$	$2,14\cdot10^{-4}$	$2,09\cdot10^{-1}$	8,15	19,92	—
$2UN+4C=2UC_2+N_2$	$2,46\cdot10^{-57}$	$1,78\cdot10^{-30}$	$1,1\cdot10^{-10}$	$8,13\cdot10^{-5}$	$2,82\cdot10^{-1}$	9,2	20	—
$2TiN+2C=2TiC+N_2$	$3,63\cdot10^{-43}$	$1,55\cdot10^{-22}$	$2,63\cdot10^{-7}$	$2,95\cdot10^{-2}$	—	9,22	15,23	—
$2ZrN+2C=2ZrC+N_2$	$8,32\cdot10^{-56}$	$3,89\cdot10^{-27}$	$3,09\cdot10^{-11}$	$2,63\cdot10^{3}$	—	29,75	23,45	298—500
	—	—	—	—	—	—	15,23	500—1000
	—	—	—	—	—	—	5,52	1000—1500
$2VN+C=V_2C+N_2$	$4,57\cdot10^{-65}$	$2,95\cdot10^{-18}$	—	—	—	59,08	30,68	—
$2VN+2C=2VC+N_2$	$6,17\cdot10^{-61}$	$1,7\cdot10^{-33}$	$5,5\cdot10^{-12}$	$3,47\cdot10^{-6}$	$8,32\cdot10^{-3}$	8	20,5	—
$2NbN+C=2Nb_{0,5}C+N_2$	$1,07\cdot10^{-44}$	$2,24\cdot10^{-23}$	$4,9\cdot10^{-8}$	$3,63\cdot10^{-3}$	—	6,35	25,85	—
$2NbN+2C=2NbC+N_2$	$5,25\cdot10^{-37}$	$7,94\cdot10^{-13}$	$9,12\cdot10^{-2}$	$2,04\cdot10$	—	4,35	10,46	—
$2TaN+C=Ta_2C+N_2$	$1,48\cdot10^{-42}$	$2,24\cdot10^{-20}$	$2,09\cdot10^{-11}$	$2,19\cdot10^{-5}$	$1,1\cdot10^{3}$	7,25	10,83	—
$2TaN+2C=2TaC+N_2$	$2,57\cdot10^{-31}$	$5,76\cdot10^{-10}$	$8,92\cdot10^{-3}$	$2,14\cdot10$	$2,69\cdot10^{3}$	4,45	9,22	—
$2Cr_2N+{}^{24}/_{23}C=$ $={}^4/_{23}Cr_{23}C_6+N_2$	$1,12\cdot10^{-17}$	$6,31\cdot10^{-6}$	$4,27\cdot10^{-1}$	$1,15\cdot10$	—	1,77	10,2	298—500
	—	—	—	—	—	—	1,76	500—100
	—	—	—	—	—	—	+0,53	1000—1500
$2Cr_2N+{}^{13}/_7C=$ $={}^4/_7Cr_7C_3+N_2$	$1,66\cdot10^{-12}$	$1,38\cdot10^{-4}$	$3,31\cdot10$	$3,63\cdot10^{3}$	—	6,00	5,00	—
$2Cr_2N+{}^3/_2C=$ $={}^4/_3Cr_3C_2+N_2$	$1,1\cdot10^{-20}$	$2,51\cdot10^{-9}$	$3,09\cdot10^{-1}$	$2,86\cdot10$	—	6,2	8,00	—
$2CrN+{}^{13}/_{23}C=$ $={}^2/_{23}Cr_{23}C_6+N_2$	$2,57\cdot10^{36}$	$2,88\cdot10^{-12}$	4,27	$2,69\cdot10^{3}$	—	12,4	11,6	—
$2CrN+{}^6/_7C=$ $={}^2/_7Cr_7C_3+N_2$	$1,41\cdot10^{-24}$	$1,35\cdot10^{-10}$	$3,72\cdot10$	$1,85\cdot10^{3}$	—	14,25	10,5	—
$2CrN+{}^3/_2C=$ $={}^2/_3Cr_3C_2+N_2$	$7,59\cdot10^{-29}$	$6,31\cdot10^{-13}$	3,55	$4,57\cdot10^{3}$	—	15	12,45	—
$2Mo_2N+2C=2Mo_2C+N_2$	$1,29\cdot10^{-22}$	$4,47\cdot10^{-10}$	$2,57\cdot10^{-1}$	$1\ 23\cdot10^{3}$	$3,92\cdot10^{3}$	14,63	8,43	—
$Mn_6N_2+{}^3/_2C={}^3/_2Mn_6C+N_2$	$6,17\cdot10^{-24}$	$2,19\cdot10^{-11}$	—	—	—	7,92	8,30	—
$Mn_6N_2+{}^{13}/_7C=$ $={}^3/_7Mn_7C_3+N_2$	$8,7\cdot10^{-32}$	$1,12\cdot10^{-13}$	—	—	—	14,52	13,45	—
$Mn_6N_2+C=Mn_6C+N_2$	$1,35\cdot10^{-22}$	$1,78\cdot10^{-11}$	—	—	—	6,00	8,45	—
$Mn_3N_2+{}^3/_7C=$ $={}^3/_7Mn_7C_3+N_2$	$6,96\cdot10^{-29}$	$5,88\cdot10^{-13}$	—	—	—	12,45	12,45	—
$2Fe_4N={}^3/_2C={}^3/_2Fe_3C+N_2$	$1,91\cdot10^{-9}$	$5,13\cdot10^{-2}$	$1\cdot10^{4}$	—	—	8,2	5,75	—
$2Fe_4N+4C=4Fe_2C+N_2$	$1,7\cdot10^{-6}$	$4,57\cdot10^{-1}$	$7,41\cdot10^{3}$	—	—	8, 2	4,98	—
$^6/_5Fe_4N+{}^4/_5C=$ $={}^3/_5Fe_3C+N_2$	$1,35\cdot10^{-1}$	$1,51\cdot10^{3}$	$3,31\cdot10^{4}$	—	—	7,98	+2,5	—
$2BN+{}^1/_3C={}^1/_3B_6C+N_2$	—	—	—	$2,13\cdot10^{-3}$	$1,7\cdot10^{-1}$	8,7	1,55	—
$2AlN+{}^3/_2C={}^1/_2Al_2C_3+N_2$	$9,12\cdot10^{-61}$	$2,45\cdot10^{-30}$	$1,2\cdot10^{-10}$	—	—	14,46	30,23	—
$^1/_3Si_3N_4+{}^3/_5C={}^3/_5SiC+N_2$	$1,86\cdot10^{-44}$	$1,95\cdot10^{-23}$	$5,89\cdot10^{-8}$	$8,32\cdot10^{-3}$	$4,68\cdot10$	0,5	15,75	298—1500
	—	—	—	—	—	—	0,38	1500—2000

In the interaction of nitrides with carbon the corresponding carbides will be formed and gaseous nitrogen will be liberated. The thermodynamic possibility of the occurrence of a reaction and its variation with an increase in temperature depends on the resultant balance of the variation with temperature of the thermodynamic stability of the products and the initial reaction components. Thus, it is possible to expect that in a region of low temperatures of the interaction reactions of nitrides with carbon will be thermodynamically improbable. With an increase in temperature the process of the interaction of nitrides with carbon occurs spontaneously, i.e., the nitrides in the carbon medium are thermodynamically unstable, and move in the direction of the formation of the corresponding carbide and gaseous nitrogen.

Actually, the data obtained by us on the calculation of the isobaric-isothermic potential [Gibbs free energy] of the interaction reaction of nitrides with carbon (Fig. 28, see Table 27) show that the pressure of nitrogen increases with an increase in temperature.

From a consideration of the lines log p - 1/T it follows that the variation in the free energy of the reaction and accordingly the pressure of nitrogen increase with an increase in temperature, i.e., the thermodynamic stability of the nitrides in the presence of carbon decreases. From a consideration of the condition $\Delta Z^0_T = 0$ (K = 1) (the condition of the impossibility of the occurrence of reaction) it follows that at certain completely definite temperatures of the interaction reactions of nitrides with carbon becomes thermodynamically improbable. The corresponding temperatures calculated by us, responding to condition $\Delta Z^0_T = 0$, are different for all nitrides and usually increase with a decrease in the valence of the metal, forming the nitride.

Thus, from an analysis of lines log p - 1/T it follows that the thermodynamic stability of nitrides in a carbon medium decreases with an increase in the atomic number of the metal group, forming the nitride.

Fig. 28. The temperature dependence of the equilibrium pressure of nitrogen of the interaction of nitrides with carbon (the numbers of the curves correspond to the numbers of the reactions in Table 27).

From Fig. 28 it is clear that according to their stability with respect to carbon all nitrides form several definite groups. The highest thermodynamic stability is characteristic of the nitrides Th_3N_4, AlN. The interaction of reactions of the nitride Th_3N_4 with carbon are characterized by the lowest values of the magnitude of pressure of nitrogen in a broad region of temperatures, thanks to which Th_3N_4 can be used in reduction media up to temperatures of

2500°K and above. Characterized by their somewhat lower stability are the nitrides of the transition metals of the fourth and fifth groups VN, UN and ZrN, and distinguished by their still lower stability are the nitrides Si_3N_4, NbN and TiN. Of all the enumerated nitrides the most thermodynamically stable with respect to carbon is, thus, thorium nitride Th_3N_4, and all the remaining enumerated nitrides can interact with carbon starting with a temperature of 1500°K.

Distinguished by their considerable instability are the nitrides of the sixth and seventh groups of the periodic system. The stability of nitrides decreases in the following sequence: CrN, Mo_2N, Mo_5N_2 and Cr_2N. Chromium mononitride is stabler than its lower nitride Cr_2N. The most stable in this group is the nitride Ca_3N_2.

In contrast to the nitrides of the preceding group for the enumerated nitrides at 100°C and above the process of interaction with carbon can be thermodynamically probable (p_{N_2} at 1000°C $\approx$ 1 at).

The latter group of nitrides is composed of the iron nitrides Fe_4N and Fe_2N, which are characterized by the absence of any stability in the presence of carbon and at comparatively low temperatures (higher than 500°C) can interact with carbon. The iron Fe_2N nitride is thermodynamically unstable in the presence of carbon even at temperatures of the order of 300°K.

Thus, from a consideration of thermodynamic data for nitride-carbon systems it follows that at temperatures, exceeding 1500°K, all examined nitrides, with the exception of Th_3N_4, are thermodynamically unstable and can intensively interact with carbon. The temperatures of the beginning of interaction (or, more exactly, of intense interaction) are different and vary considerably from one nitride group to another.

4. The Classification of Nitrides

Analysis of the properties and the electronic structure of nitrides makes it possible to propose a classification for them based on

unique principles [859, 860]. This classification, naturally, ensures from a classification of the elements of the periodic system into s-, ds-, fds-metals and sp-elements (nonmetals and semimetals).

The first class includes nitrides of electropositive metals of groups I and II of the periodic system, the atoms of which have external s-electrons with completely vacant or completely filled deep-lying shells (in a state of isolated atoms). These nitrides have compositions, corresponding to the usual valences, are characterized by the transfer by the metal atoms of valence electrons to the nitrogen with the formation of stable s^2p^6-configurations by both components (metal and nitrogen) or d^{10}- and s^2p^6-configurations which determines their ionic character, manifested externally in hydrolysis by the liberation of ammonia, high electric resistance, and semiconductor properties. Along with the strong and clearly expressed Me-N ionic bonds these nitrides are also characterized by covalent component of bonding, mainly, between the metal atoms (in nitrides) and the nitrogen atoms (in azides). This class of nitrides with respect to the type of chemical bond can be called the ionic-covalent nitride class.

It is necessary to note that the relationship of these two types of bonds in the nitirdes of the indicated class differs rather greatly; for certain nitrides attributes of metallic bonding also appear, for example, for nitirdes of the alkali earth metals.

The second class includes nitrides, formed with sp-elements, i.e., nonmetals and semimetals. For them the formation by both components of stable sp-configurations is characteristic, which in proportion to the increase in their energetic stability are isolated from each other in an energetic regard. This causes the anpearance of energy gaps between the nonmetal and nitrogen atoms and corresponding semiconductor or dielectric properties. Basically they correspond to the usual valence formulas; the bonds between the atcms in the crystal lattices are directional, rigid, and of the covalent type, – which determines absence in them of regions of homogeneity. This class of nitrides can be called the covalent nitride class.

The third class includes transition-metal nitrides with filled d- and f-electron shells. The nitrides of this class are characterized by more or less broad regions of homogeneity, by mainly metallic properties, high electric conductivity, high melting points, and hardness. The nitrides of this class are formed from elements with considerable liberation of heat and are the result of such a redistribution of the valence electrons of the metal and nitrogen, which leads to the formation of the maximum statistical weight of atoms, possessing stable configurations of a localized part of valence electrons. For transition-metal nitrides the presence of a strong covalent bond between the metal atoms is characteristic, and also mainly of a metallic bond between the metal and nitrogen atoms which makes it possible to include them in the covalent-metallic nitride class.

The range of variation in the physical properties within this class of nitrides is extraordinarily broad. Along with the mainly metal-like nitrides within this class there is a group of nitride phases, in which the covalent bond predominates, and a certain fraction of ionic bond also appears. Such phases possess semiconductor properties, but with characteristic properties, which are inferior to the properties of the typically covalent nitrides.

This classification has an arbitrary character, since it is impossible to draw sharp and clear boundaries between any classes of nitrides. The properties, the electronic structure and the types of chemical bonding of nitrides vary discretely, i.e., with the transition from nitride to nitride a single general line and direction of the variation of the electronic structure and properties exists corresponding to the same variation in the properties of chemical elements, forming nitrides [861].

C H A P T E R II

METHODS OF PREPARING NITRIDES

The most important methods of preparing nitrides are: 1) the direct action of nitrogen, ammonia or other gaseous nitrogen-containing compounds on elements or their hydrides; 2) the reduction of oxides in the presence of nitrogen, ammonia; 3) the thermal dissociation of compounds, containing a given element and nitrogen; 4) the precipitation of nitrides from the gas phase.

The direct interaction of elements with nitrogen is accomplished by the action of nitrogen, ammonia or other gaseous nitrogen-containing compounds on the powders of metals and nonmetals or on solid metals, or on the hydrides.

The interaction reaction between elements (Э) and nitrogen is described by the equation

$$2Э + N_2 \rightleftarrows 2ЭN.$$

In spite of the high dissociation energy of the nitrogen molecule (225 kcal/mole [734]), its use for nitridation is more preferable than ammonia. This is explained by the fact that the hydrogen forming upon the dissociation of ammonia, although it is a reducing agent, removing from oxide films a surface, it can form with many elements, especially metals, relatively stable hydrides. Thus, to remove the hydrogen and to replace it with nitrogen an additional expenditure of energy is necessary that is expressed in

higher formation temperatures of nitrides. For example, in the nitridation of transition metals by the action of ammonia complex interstitial phases of nitrogen and hydrogen will be formed in the spaces between the metallic atoms [735], the so-called nitridehydrides, the removal from which of hydrogen occurs at higher temperatures than from normal hydrides. Thus, with the action of nitrogen on zirconium powder, zirconium nitride ZrN will be formed in the course of 1-2 h at a temperature of 1200°C, and when the action of ammonia zirconium nitride with a saturated content of nitrogen can be produced only after being held for two hours at 1400°C [178]. The same was observed with the use instead of the metals of their hydrides. Thus, at 500-800°C, when titanium hydride is rather stable the nitrogen content in the nitridation product is two times less than in unhydrided titanium powder, nitridated under the same conditions. At 1000°C, when titanium hydride noticeably dissociates, saturation with nitrogen occurs more intensively and the maximum saturation with nitrogen is attained at 1200°C in the course of 2-4 h, i.e., under the same conditions, as for pure titanium. It follows from this that in general the nitridation of hydrides occurs more readily than the treatment of pure metals with ammonia, i.e., under the conditions, when complex interstitial phases of the nitride-hydride type will readily be formed.

In many cases nitridation more perferably occurs with ammonia, which is able with certain metals to form amides, which are readily transformed in the corresponding nitrides [6]. Thus, alkali metals even at normal temperature and especially rapidly with heating dislodge one atom of hydrogen from the ammonia molecule with the formation of amides of the metals

$$2\,Me + 2\,NH_3 \rightarrow 2\,MeNH_2 + H_2.$$

The alkali earth metals form amides with great difficulty and only with heating.

Upon heating the amides decompose with the formation of nitrides

$$3NaNH_2 \rightleftharpoons Na_3N + 2NH_3,$$

and the amides of alkali metals decompose with much more difficulty than those of the alkali earth metals.

The mechanism of a nitridation reaction in general reduces to the diffusion of nitrogen in the depth of a metal or a nonmetal (with the formation of a solid solution). After achieving a definite temperature normal heterodiffusion changes to reactionary diffusion with the formation of nitride phases. The formation rate of a nitride is limited by rate of the reaction and by the diffusional transmission of nitrogen through the layer of an already formed nitride. The mechanism of the nitridation process is analogous to the mechanism of the oxidation process [76], however, as a rule, the rate of nitration is less than the rate of oxidation. This can be explained by the fact that whereas oxygen, an isolated atom of which has an s^2p^4 configuration of valence electrons, tends to be filled to a stable s^2p^6-configuration as the only one possible (with transformation into an O^{2-} ion), for a nitrogen atom (the configuration of the valence electrons is s^2p^3) there is both the tendency to complete the s^2p^6-configuration, and also the probability of giving up one electron with the formation sp^3-configurations, which serves as a factor, delaying diffusion as compared to oxygen [1070]. For the same reason the reaction rate constant of nitridation increases in proportion to the reduction in the statistical weight of the non-localized electrons (Table 28) [178].

Table 28. Reaction rate constants of the nitridation of powders certain transition metals, $g/cm^3 \cdot s$.

Temperature °C	Ti–N	Zr–N	V–N	Nb–N	Ta–N	Cr–N
500	$5{,}68 \cdot 10^{-6}$	$8{,}22 \cdot 10^{-6}$	$1{,}7 \cdot 10^{-5}$	$2{,}21 \cdot 10^{-5}$	$2{,}47 \cdot 10^{-2}$	$1{,}08 \cdot 10^{-1}$
600	$2{,}20 \cdot 10^{-5}$	$4{,}1 \cdot 10^{-5}$	$2{,}95 \cdot 10^{-5}$	$3{,}79 \cdot 10^{-5}$	$7{,}28 \cdot 10^{-2}$	$2{,}51 \cdot 10^{-1}$
700	$1{,}65 \cdot 10^{-5}$	$6{,}8 \cdot 10^{-5}$	$3{,}72 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$1{,}58 \cdot 10^{-1}$	$5{,}27 \cdot 10^{-1}$
800	$3{,}33 \cdot 10^{-5}$	$8{,}3 \cdot 10^{-5}$	$5{,}8 \cdot 10^{-5}$	$1{,}1 \cdot 10^{-4}$	$1{,}5 \cdot 10^{-3}$	$3{,}39 \cdot 10^{-1}$
900	$8{,}0 \cdot 10^{-5}$	$5{,}2 \cdot 10^{-5}$	$1{,}8 \cdot 10^{-4}$	$1{,}4 \cdot 10^{-4}$	$1{,}1 \cdot 10^{-2}$	$7{,}24 \cdot 10^{-1}$
1000	$4{,}1 \cdot 10^{-4}$	$1{,}01 \cdot 10^{-4}$	$2{,}3 \cdot 10^{-4}$	$2{,}3 \cdot 10^{-4}$	$3{,}35 \cdot 10^{-4}$	$5{,}88 \cdot 10^{-1}$
1100	$7{,}47 \cdot 10^{-4}$	$2{,}2 \cdot 10^{-4}$	—	$4{,}3 \cdot 10^{-4}$	$8{,}25 \cdot 10^{-4}$	$6{,}28 \cdot 10^{-1}$
1200	$7{,}47 \cdot 10^{-4}$	$2{,}2 \cdot 10^{-4}$	$3{,}71 \cdot 10^{-4}$	$6{,}11 \cdot 10^{-3}$	—	$4{,}55 \cdot 10^{-1}$

Consequently, to accelerate the process of nitride formation maximum pulverization of particles of the powder is necessary. However, when the tendency toward surface oxidation exists, simultaneously with the pulverization the relative content of oxygen in the powder increases and nitridation is hampered. Thus, in each individual case a certain optimum size of particles should be selected.

Of great importance is the maximum development of the reaction surface with the formation in the process of nitridation of nitrides with covalent type bonds and following from this with a low transfer rate of nitrogen atoms (BN, AlN). In this case from the greatest surface deveopment special "linings" or "carriers" are used from substances, possessing a high free surface. Such type of substances include chalk, calcium phosphate and many other substances, which decompose upon heating with the liberation of gaseous components, bringing about their intense loosening, the formation of a thin, openwork structure with a high surface. The lining can also be under certain conditions the obtained nitride itself with the formation by it of very thin particles (for example, the production of aluminum nitride by nitridation of aluminum powder, mixed with a nitride; the same in producing boron nitride).

Analogous measures are taken in those cases, when the temperature of nitridation is higher than the melting point of the metal and the reaction surface is sharply limited by the molten surface, as is observed in obtaining gallium and indium nitrides. The metal being nitrided is mixed with a substance, which actively decomposes upon heating, for example, with ammonium carbonate. Upon decomposition of the latter ammonia and CO_2 are liberated, loosening and mixing the melt, facilitating the admission of nitrogen; furthermore, ammonia produces an additional nitriding effect.

On the other hand, the nitridation of certain relatively fusible metals upon the formation of the molten metal occurs more rapidly than in the solid state. Nitridation moreover occurs spasmodically,

approximately at the melting point of the metal. This is explained by the disturbance of (upon melting of the thinest and nitrogen-quasiimpermeable) the nitride film. Obviously, the formation of the nitride occurs in the short interval of time of melting before the formation of a continuous surface of molten metal.

Table 29. The value of the ratios of the heats of formation of nitrides to the heats of fusion of the corresponding metals.

Property	Al.	La	Ce	Ti	Zr	V	Ta	Mo
Latent heat of fusion $Q_{пл}$, cal/g	93	19,4	13	90	60	80	37	60
Heat of formation of the nitride $Q_{обр}$, cal/g	1820	472	500	1350	730	930	308	80
$Q_{обр}/Q_{пл}$	19,6	24,3	38,4	15	12,8	11,6	8,4	1,34

If the heat of fusion of the metal being nitrided is substantially less than the heat of formation of the nitride (Table 29), then the reaction mass is sharply heated, for example in the nitridation of metallic cerium and lanthanum, and also aluminum.

This factor also determines the high reaction rate and, probably, should be considered in all cases of nitridation, when on the metal surface a quasi-impermeable (for gases) film forms. This type of film can be disturbed during nitridation under pressure, as is observed, for example, in obtaining aluminum nitride from aluminum powder [590]. Furthermore, nitridation under pressure frequently makes it possible to intensify the process of the formation of nitride phases (the reaction rate of nitridation increases approximately proportionally to the square root of the pressure).

Besides the indicated example of the nitridation of niobium in [590], this method was used in the nitridation of niobium in [295]. The device for the nitridation of niobium under pressure up to 240 at is shown in Fig. 29.

Supernigh pressures are used only in individual cases, for

example in producing the cubic modification of boron nitride (borazon) from hexagonal BN of the graphite type. For this pressures of the order of 40-70 thousand at are used and equipment, analogous to the devices for producing artificial diamonds.

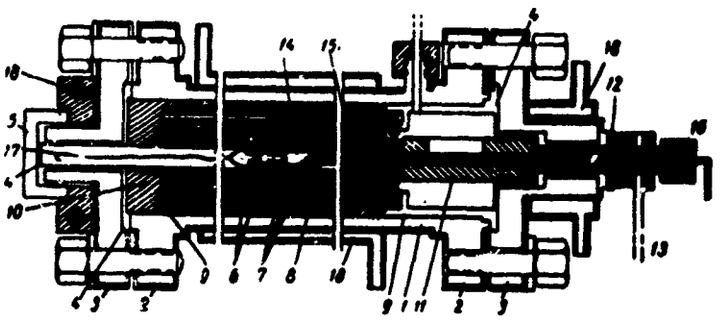


Fig. 29. A device for the nitridation of niobium under pressure: 1 - steel pipe; 2 - steel flange; 3 - steel cover; 4 - sealing ring; 5 - connecting cap; 6 - corundum pipe; 7 - ceramic pipe from pythagorean mass; 8 - molybdenum band; 9 - centering component of brass; 10 - springy copper plate for contact; 11 - current supply; 12 - insulating bushing; 13 - current supply cable; 14 - container with the substance; 15 - thermocouple in a protective tube; 16 - connecting cap with lead-in for thermocouple; 17 - platinum wire; 18 - cooling jacket.

As was indicated in [1047], of great importance in the direct nitridation of powders is the rate of heat removal from the reaction space. At a slow removal rate the temperature of the sample is sharply increased and the reaction rate of nitridation increases, i.e., thermal ignition occurs, as a result of which the powder is severely baked or melted which, in turn, impairs gas permeability and the conditions of nitridation. It has been established that the addition of nitrides to metallic powders very significantly increases their ignition point in nitrogen, smooths the temperature effects at the time of ignition, promotes improvement in the gas permeability of the charge and in the technological properties of the intermediate and end products of nitridation.

The production of nitrides of refractory metals, aluminum and magnesium by the nitridation of powders under industrial conditions [843] was carried out by the continuous method, i.e., with the continuous supply of powder into the heating zone of the furnace in an atomized (suspended) state. This makes it possible to increase by approximately 50 times the productivity of the furnaces as opposed to periodic loading, and also to obtain nitrides not in form of sintered masses, but in form of powders which practically eliminates subsequent pulverization and makes the process less expensive.

Recently attempts have been made to obtain nitrides by the atomization of metals in a plasma stream with the application of nitrogen. Thus, in [950] magnesium and titanium nitrides were synthesized by treating metals in a plasma stream of nitrogen. The obtained products contained 30-40% of the corresponding nitrides. With the analogous treatment of tungsten and molybdenum nitrides will not be formed. In principle the same method can be used to obtain complex nitrides - in treating borides by a plasma stream metal nitrides or boronitrides will be formed: complex compounds with nitrogen with the treatment of silicides and carbides will also be formed [951, 952].

The reduction of oxides in the presence of nitrogen with the formation of nitrides occurs according to the reaction

$$MeO + Me(X) + N_2 \rightarrow MeN + MeO(XO),$$

where Me is the metal-reducing agent, X is the nonmetallic reducing agent (carbon, silicon, boron, etc.).

The usual reducing agent is carbon. However, in the reduction of oxides of carbide-forming metals along with a nitride a carbide will also be formed, which can yield with the nitride a continuous series of solid solutions, as occurs in the production of titanium nitride, where the solid solution TiN – TiC (or TiN – TiC – TiO) will

be formed [110]. This limits the possibilities of using the method mainly to the production of technical nitrides, if the contamination by carbon does not substantially affect their subsequent use.

The peculiarities of producing nitrides by the reduction of metal oxides with carbon with simultaneous nitridation were investigated using as an example titanium and niobium nitrides [1047]. It was demonstrated that with an increase in temperature and a reduction in the nitrogen pressure the carbide content in MeC – MeN equilibrium solid solutions is increased. Thus for the production of titanium and niobium nitrides, minimumally contaminated with carbon, it is necessary to carry out the reactions at the lowest possible temperatures and at increased nitrogen pressures. A substantial effect on the rate of reduction and nitridation is rendered by the diffusion of carbon monoxide and nitrogen into the pores of the compressed charge (the degree of this effect depends on the radius of the pores and the geometric dimensions of the briquets of the compressed charge). The restoration reaction of a metal oxide with carbon and the saturation of the reduced metal with nitrogen occurs mainly within the pores of the charge, i.e., it is connected with the removal of the carbon monoxide and with influx of nitrogen to the site of the reaction. If the rate of circulation of carbon monoxide and nitrogen in the pores is greater than the rate of the reaction, then efficient reaction rates will occur. The delayed diffusion of carbon monoxide and low nitrogen pressure which delays the formation reaction of the nitride, and shifts it in the direction of the formation of carbide. It has been established that the mechanism of the transfer of carbon monoxide and nitrogen into the pores of the charge and the intermediate reaction products is determined by a Knudsen regime, for which a small diameter of the pores as compared to the length of the free path of the molecules is characteristic, and also a low coefficient of diffusion, as a result of which a large gradient of pressures of carbon monoxide and nitrogen is created with respect to the cross section of the briquet of the charge. Under Knudsen conditions the flow of molecules through a capillary with length Δx and radius r is described by the equation

$$\frac{dn}{dt} = \frac{8}{3} \cdot \frac{\pi r^3}{\sqrt{2\pi mKT}} \cdot \frac{\Delta p}{\Delta x},$$

where dn/dt is the molecular flow per second; m is the molecular mass; K is the Boltzmann constant; T is the temperature $\Delta p/\Delta x$ is the pressure gradient in a pore.

The calculated values of the radius of pores of the initial compressed charges in producing titanium and niobium nitrides were equal to 400-500 Å with an overall porosity of 47 % and the calculated radii of the pores of the intermediate reaction products are within the limits of 3000-5000 Å with overall porosity of 60-80%, where with an increase in reaction time the values of radii of the pores and total porosity increase. Proceeding from this, it was shown that the flow rate of molecules of carbon monoxide and nitrogen in the pores of the intermediate and end reaction products at identical gradients of pressures was several orders greater than in the pores of the initial charge. Due to the low rate of Knudsen molecular flow in the pores of the initial charge in the first reaction stage the greatest partial pressure of carbon monoxide is created and the reaction is slowed down, and the external crust of the intermediate product or nitride formed during the reaction on the surface of the briquet practically does not create an additional gradient of pressure, and the reaction front with the passage of time shifts toward the center of the briquet, i.e., the reaction does not proceed with respect to the whole volume simultaneously, but shifts from the periphery to the center, where the rate of increase in the thickness of the nitride crust (layer) obeys the linear law $\Delta x = k\tau$, where τ is time.

A calculation of the equilibrium and kinetic peculiarities of the course of reductions-nitridation reactions makes it possible to establish the optimum conditions for producing of titanium and niobium nitrides which are respectively, temperatures of 1250 and 1400°C, a nitrogen pressure of $4 \cdot 10^5$ N/m^2, a nitrogen flow rate of 0.18 m/s, a heating period of 3 and 4-5 h (for charges, granulated into pellets

with a diameter of 13 mm). The niobium and titanium nitrides, obtained under these conditions, contain respectively, 12.9 and 21.5% nitrogen with the absence of carbon in the niobium nitride and a nitrogen content of 0.5-0.7% in the titanium nitride.

As a reducing agent not only carbon and other nonmetals are used, but also metals - calcium, magnesium or their hydrides. The authors [192] developed methods of producing titanium, zirconium and tantalum nitrides according to the following schemes

$$TiO_2\,(Ta_2O_5) + CaH_2 \rightarrow Ti\,(Ta) + H_2O + CaO,$$
$$2Ti\,(Ta) + N_2\,(2NH_3) \rightarrow 2TiN\,(TaN) + (3H_2)$$

or

$$ZrO_2 + 2Mg - Zr + 2MgO,$$
$$2Zr + N_2\,(NH_3) \rightarrow 2ZrN + (H_2).$$

This method was analyzed in detail with respect to the producing of zirconium nitride [251]. Certain difficulties of its use are shown, connected with the fact that in proportion to the reduction of zirconium dioxide by magnesium and the transition in the region of the solid solution of oxygen to zirconium level of the binding energy substantially increases and the removal of the remaining oxygen requires the selection of a corresponding regime of the reduction and its careful control. The reduction process passes, apparently, through the stage of the formation of magnesium nitride Mg_3N_2.

The reduction temperatures of oxides with the use of metals or their hydrides as reducing agents are usually 800-1200°C; for carbon they are higher (for example, for the formation of titanium nitride - 1600-1700°C).

In certain cases the reduction of oxides with the formation of nitrides is accomplished directly with ammonia, the hydrogen

of which plays the role of the reducing agent. For example, by this method it is possible to produce copper nitride

$$3Cu_2O + 2NH_3 \rightarrow 2Cu_3N + 3H_2O.$$

According to [1024], there is indicated the possibility of a sharp reduction in reduction temperatures and nitridation temperatures with the use of freshly precipitated hydroxides, which are treated with mixtures of ammonia and hydrogen.

Thermal dissociation is carried out with the application of compounds, simultaneously containing a metal and nitrogen. Thus aminochlorides can be used, for example

$$TiCl_4 \cdot 4NH_3 \rightarrow TiN + NH_3 + HCl$$

or complex ammonium fluoride compounds of the type $(NH_4)_xMeF_y$ [274], upon the decomposition of which (at 300-800°C) corresponding nitride phases will be formed. This method makes it possible to produce the nitrides AlN, VN, NbN, Ta_3N_5, CrN, U_3N_4, Fe_2N, however manganese, beryllium, zinc, titanium, zirconium nitrides either cannot be produced by this method or they can be with difficulty.

Since a metal enters into the composition of compounds already in the ionized state, then with delicate decomposition frequently nitrides will be formed, approaching the composition, which is determined by the ionic bonding components of these compounds. This, in particular, was observed in the formation of titanium nitride from aminochlorides, when it was possible to obtain the nitride of the composition $TiN_{1.16}$, and also in the preparation of tantalum nitride from $(NH_4)_2TaF_7$, which leads to the formation of Ta_3N_5. In the direct nitridation of metals the formation of these types of metastable phases with hypertrophied fractions of an ionic bonding is practically never observed.

Included in this group of production methods is the thermal

decomposition of amides and imides, described above, and also the thermal dissociation of the higher (with respect to nitrogen content) nitride phases with the formation of the lower ones. It is necessary to note that in the latter case it is fairly difficult to produce a nitride of a definite phase composition, i.e., pure nitride phases without impurities of the higher phases (in case of transition-metal, the highest nitrides of the nontransition metals - azides - decompose with the formation of phases of a strictly definite composition).

The precipitation of nitrides from the gaseous phase was used long ago in diverse variants, and at the present time is acquiring especially great importance in connection with the possibility of producing in this manner single-crystal and pure nitrides.

An example of this method is the interaction of chlorides or oxychlorides of metals with ammonia, which can be represented by the followihg schemes:

$$MeCl_4 + NH_3 \rightarrow MeN + HCl.$$
$$MeOCl_3 + NH_3 \rightarrow MeN + H_2O + HCl.$$

These reactions usually occur at temperatures of the order of 800°C. In this manner titanium [736], vanadium [737], chromium and other transition metal nitrides are obtained [257].

Below (Table 30) the conditions of the precipitation of nitrides with the interaction of chlorides with a nitrogen-hydrogen mixture are given.

Table 30. Conditions of the precipitation of nitrides from the gaseous phase.

Nitride	Initial chloride	Nitriding agent	Precipitation temperature, °C
TiN	$TiCl_4$	$3N_2+H_2$	1100—1700
ZrN	$ZrCl_4$	$3N_2+H_2$	1100—2700
ZrN	$ZrCl_4$	N_2	2800—3000
HfN	$HfCl_4$	$3N_2+H_2$	1100—2700
VN	VCl_4	$3N_2+H_2$	1100—1600
TaN	$TaCl_5$	N_2	2400—2600

A thermodynamic investigation of the conditions of the precipitation of nitrides from the gaseous phase and for the precipitation of titanium nitride by iron was conducted [157].

$$TiCl_4 + {}^1/_2 N_2 \rightleftarrows TiN + 2Cl_2, \quad \text{(II.1)}$$

$$TiCl_4 + 2H_2 + {}^1/_2 N_2 \rightleftarrows TiN + 4HCl, \quad \text{(II.2)}$$

$$TiCl_4 + 2Fe + {}^1/_2 N_2 \rightleftarrows TiN + 2FeCl_2. \quad \text{(II.3)}$$

The dependence of the decrease in free energy on temperature is expressed by the corresponding equations

$$\Delta F_1 = 96100 - 6{,}7T,$$

$$\Delta F_2 = 7500 - 13{,}45T,$$

$$\Delta F_3 = 51300 - 34{,}2T.$$

The completeness of the course of reactions (II.1) and (II.2) increases with an increase in the temperature of precipitation; reaction (II.3) above 1100°C becomes inefficient.

The preparation of articles from nitrides in principle is possible by various methods, of which the basic ones are: 1) the sintering of intermediate products, compressed from previously produced nitride powders; 2) the hot compressing of nitride powders; 3) reaction sintering; 4) the casting of articles from nitrides.

The sintering of intermediate products, compressed from a nitride powder, can be accomplished in a nitrogen medium, nitrogen-containing reducing gases or in a vacuum. In the latter case a certain loss of nitrogen occurs (of the order of several tenths of a percent), however at definite temperature regimes this loss can be reduced to a minimum with the simultaneous producing of sufficiently dense (a porosity of 0-2%) articles [232]. Titanium, zirconium, vanadium, niobium, tantalum nitrides vary little with sintering in vacuum; on the contrary, chromium and molybdenum nitrides lose considerable amounts of nitrogen in a vacuum and it is not possible to sinter them in this way. The best results are obtained by sintering in a protective nitrogen medium.

The hot compressing of nitride powders gives satisfactory results, however a sintered article in the case of the use of the usually employed graphite molds is considerably contaminated with carbon and special measures are required to prevent this contamination (the use of nonconducting molds of nitrides, the thorough coating of the internal surface of the molds with boron or aluminum nitride, etc.).

Hot compressing should be carried out in a protective (containing nitrogen) or a neutral (argon) gaseous environment [232].

Reaction sintering - the combination of the processes of nitride formation and their sintering - frequently gives the most favorable results [740]. In this case due to the formation of new phases and the increased activity of the atoms or atomic complexes the processes leading to shrinkage and compaction of the articles as compared to ordinary sintering of the preliminarily compressed intermediate products from the powders of the previously produced compounds are sharply intensified. The specific volume of the phase formed during nitridation is larger than the specific volume of the original metal which leads to a reduction in the porosity of the sintered intermediate product due to the purely volume factor. From a comparison of the atomic volumes of metals and the molecular volumes of the nitrides (Table 31) it follows that the increase in volume is usually considerable, and if it does not exceed the porosity of the intermediate products compressed from the metallic powder, then it is necessary to compact a briquet.

However reaction sintering alone does not make it possible to produce sufficiently low residual porosity (it is usually not lower than 10-15%) which is result of strong forces pushing apart, caused by the formation of new phases (according to Raub and Plate [738]). Therefore after reaction sintering additional sintering is necessary with hot pressing [739], which leads to the production of articles with low residual porosity. During hot pressing contamination of the article occurs due to the material of the mold, since the

possibilities of the penetration of these impurities into a preliminarily sintered briquet sharply are reduced as compared to hot pressing of a powder. In Table 32 the recommended regimes of operation [739] are give for this double process - reaction sintering with subsequent hot pressing.

Table 31. A comparison of the atomic volumes of metals and the molecular volumes of their nitrides.

Nitride	Atomic volume of the metal, cm^3	Molecular volume of nitride, cm^3	Variation in volume, %
TiN	10,6	11,4	+7,5
ZrN	14,03	14,8	+5,5
HfN	13,64	13,9	+1,9
V_2N	8,36	10,8	+29,3
VN	8,36	10,7	+28,0
Nb_2N	10,8	12,9	+19,2
NbN	10,8	12,8	+18,5
Ta_2N	10,9	12,2	+12
TaN	10,9	12,7	+16,5
Cr_2N	7,23	10,1	+39,5
CrN	7,23	10,8	+49,3
Mo_2N	9,40	13,6	+45

Table 32. Conditions of producing compact samples.

Compound	Simultaneous nitridation and sintering			Additional sintering by the hot compression method		
	Compression pressure, t/cm^2	Temperature °C	Pressure period, min	Compression pressure, kg/cm^2	Temperature °C	Pressure period, min
TiN	2,0	1200	240	150	2300	3
ZrN	1,8	1200	240	150	2300	3
HfN	1,8	1200	240	150	2300	3
V_2N	1,8	900	480	100	1850	3
VN	2,3	1300	240	100	1800	3
Nb_2N	1,8	900	480	100	1850	3
$NbN_{0,75}$	2,0	1100	480	—	—	—
$NbN_{0,97}$	1,8	1100	480	—	—	—
NbN	2,3	1200	240	100	1800	3
Ta_2N	3,0	900	900	480	1850	3
TaN	3,0	1200	240	100	1800	3
Cr_2N	1,8	1300	240	—	—	—
CrN	2,0	950	240	—	—	—
Mo_2N	1,8	700	480	—	—	—

For activation of the sintering process of nitride powders, in particular during hot pressing, small metallic additives are sometimes introduced into their composition, which create the possibility of recrystallization of the particles through liquid phase and after this are partially removed evaporation at high sintering temperatures. An example of this is the sintering of articles from uranium nitrides.

Regarding the casting of articles from nitrides, it practically is not used, with the rare exception, for example, of producing articles from uranium nitrides.

C H A P T E R III

METAL NITRIDES OF GROUP I OF THE PERIODIC SYSTEM

1. Nitrides of the Alkali Metals

Lithium nitrides. Ir the lithium- nitrogen system there has been established the existence of a nitride of the composition Li_3N; there are separate indications about the existence of the nitride (azide) LiN_3 [1]. The compound Li_2N supposedly forming during the action of nitrogen on thc nitride Li_3N was not confirmed with the carrying out of this reaction in work [2]. The phase diagram of the lithium-nitrogen system was investigated in [3] only for the $Li-Li_3N$ section (Fig. 30). In this work it was not possible to establish the nature of interaction for the section, directly adjacent to lithium. An investigation was carried out with alloys somewhat contaminated by iron which, in the opinion of the authors, caused a reduction in the melting point of the nitride to 815°C (instead of the value frequently mentioned in literature - 845°C).

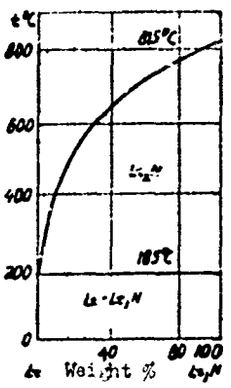


Fig. 30. A section of the phase diagram of the lithium-nitrogen system.

The usual method of preparing lithium nitride Li_3N is the action of nitrogen on metallic lithium in the cold state or with heating [24]. Dafert and Miklauz [4] established that lithium nitride will be formed by the action of dry nitrogen on lithium during the course of several hours. Upon heating the reaction is accelerated and occurs especially energetically at a temperature of 450-460°C (it is accompanied by combustion) [1.5-9]. In work [14] Li_3N was also produced by the interaction of lithium with nitrogen at a temperature of 450°C. Frankenburger [10], who investigated kinetics of the interaction of lithium with nitrogen, determined that the rate of reaction depending upon temperature is either in the kinetic, or in the diffusion region. Klinayev studied this question most completely [11], his results makes it possible to attribute the nitridation reaction of lithium to topokinetic reactions, characterized by a sharp phase border between the initial and the newly forming phases. The reaction kinetics of the nitridation of lithium at a temperature of 25°C is described by the Kolmogorov-Yerofeyev topokinetic equation,

$$\alpha = 1 - e^{-k\tau^n},$$

where α is the portion of reacting substance to time τ, k is a contant, n is integral index.

The formation rate of the nitride, according to [11], is substantially affected by additives, for example in nitridation at 25°C the addition of potassium (0.18%) to lithium accelerates the reaction, but the additions of magnesium (1.13%) or aluminum (0.53%) retard it. Sodium (1.45%) and calcium (0.38%) impurities do not noticeably affect the formation rate of lithium nitride.

Oxygen and hydrogen are inhibitors of the interaction reaction of lithium with nitrogen. Thus, the presence in nitrogen more than 14 vol.% of oxygen or more than 3.5 vol.% of hydrogen completely prevents nitridation, irrespective of the purity of the original metal.

According to [1059], it is recommended that lithium nitride be produced by the action of nitrogen on lithium under pressure for a period of 1-2 h. The temperature is gradually increased to 170-175°C, the pressure of the nitrogen - to 6-8 at; they are held under these conditions for 4-6 h, after which the product is cooled and unloaded. The yield of lithium nitride is 98-99%; the ratio of the Li:N content in the obtained nitride is 3.0 ± 0.1; the nitride is produced in the form of dark-red or brown plates; the melting point is 845°C; the density at 20°C is 1.390 g/cm^3 (see also [1071]).

Under the effect of air on lithium a mixture of nitride (75%) and oxygen compounds of lithium of indefinite composition will be formed [12]. The impurities in lithium have a substantial effect on its interaction rate with air at a temperature of 20°C (Fig. 31). An increase in atmospheric humidity (Fig. 32) and temperature also increase the nitridation-oxidation rate. Above 60°C the stability of lithium with respect to air increases (with the presence of a protective film, consisting mainly of lithium nitride).

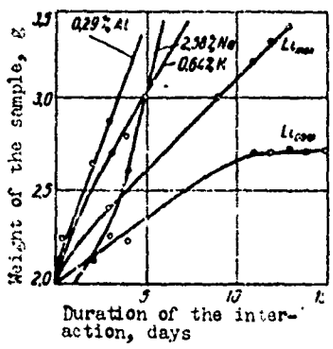


Fig. 31.

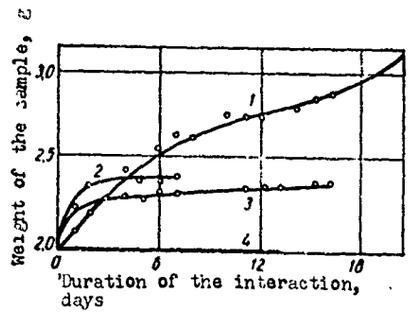


Fig. 32.

Fig. 31. The effect of impurities on the interaction of lithium with air.

Fig. 32. The interaction of lithium with air of various humidity: 1 - humidity 100%; 2 - humidity 50%; 3 - humidity 30%; 4 - dry air.

The lithium nitride, produced by the interaction of lithium with nitrogen at a temperature of 450-460°C, is a porous substance

from blue-black to violet-black in color, sometimes in transient light having a ruby-red color (mixture of Li_3N and Li_2O have the same color).

Lithium nitride has a hexagonal structure with the lattice constants, given in Table 34.

Lithium nitride changes rapidly in air (therefore it is stored in a nitrogen medium); under the effect of water it decomposes with the formation of hydroxide and ammonia

$$Li_3N + 3H_2O \rightarrow 3LiOH + NH_3.$$

Upon heating in hydrogen lithium nitride is converted to lithium hydride with the formation of ammonia. The reaction passes through intermediate stages with the formation of the amide $LiNH_2$ and the imide Li_2NH. Upon heating to a temperature of 800°C it corrodes iron, nickel, copper, platinum, quartz and porcelain [13].

With nitrides of other metals lithium nitride yields compounds of the $Li_3N \cdot MeN$ type [236]. The interaction of lithium nitride with nitrogen at temperatures of 400-500°C and at pressure of 300 at does not lead to the formation of the highest lithium nitrides [2].

In work [241] the solubility of lithium nitride in molten salts was studied (Table 33).

Table 33. The solubility of Li_3N in molten salts.

Molten salt	Temperature, °C	Li_2N, solu-moles per 1 mole of molten salt
KCl — 58,3 mole % LiCl	495—635	0,063—0,080
$LiCl_3$ — 28 mole % LiF	535—610	0,161—0,220
LiCl	620—695	0,128—0,168
LiCl — 23 mole % LiF — 21 mole % LiH	495—585	0,175—0,236
LiBr	590—665	0,11—0,126

At temperatures up to 360°C lithium nitride practically does not conduct an electric current, but with an increase in temperature to about 550°C its electric conductivity rapidly increases [14], where within the limits of 350-549°C the curve of the dependence of κ on 1/T consists of two segments, intersected at a point, corresponding to temperature 446°C, and $\kappa = 12.3 \cdot 10^{-6}\ \Omega^{-1} \cdot cm^{-1}$. The temperature dependence of electric conductivity is described by the expression $\kappa = 5.28 \cdot 10^{-2} \exp(-6196/T) + 4.3 \times 10^{7} \exp(-21700/T)$, characteristic for ionic conductivity. Upon the electrolysis of Li_3N at 480-550°C lithium is deposited on the cathode, nitrogen is given off at the anode, but on the electrodes an emf of polarization appears which proves the presence in Li_3N of the ion N^{3-}. The basic properties of lithium nitride are given in Table 34.

Table 34. The properties of nitrides and azides of the alkali metals.

Characteristic	Li_3N	LiN_3	Na_3N	NaN_3	K_3N	KN_3	Rb_3N	RbN_3	Cs_3N	CsN_3
Nitrogen content, weight, %	40,22	85,82	16,88	64,64	10,67	51,80	5,18	32,96	3,39	24,02
Crystal structure	Hexagonal	—	Rhombohedral	Hexagonal	Tetragonal	Tetragonal	—	Tetragonal	—	—
Lattice constants, kX										
a	3,658	—	—	5,488	—	6,094	—	6,36	—	—
c	3,882	—	—	—	—	7,058	—	7,41	—	—
c/a	1,061	—	—	—	—	1,158	—	1,165	—	—
$\alpha°$	—	—	—	38°43′	—	—	—	—	—	—
Specific gravity	1,28	—	1,846	1,838	—	2,056		2,788	—	
Melting point, °C	845	—				343		321	—	326
Decomposition temperature, °C			300	275	—	355		395	—	390
Heat of formation, kcal/mole	—49,5	2,6*	—3,6*	5,1*	20*	—0,3*	43*	—0,1*	75*	—2,4*
Heat capacity, cal/g·deg	$11,73+23,0 \cdot 10^{-3}T$	—	19,1 (273—373°K)	—	—	—	—	—	—	—
Lattice energy, kcal/mole*	1221	194	1127	175	1005	157	964	152	911	146
Free energy, kcal/mole	[illegible]—37	—	—	—	—	—	—	—	—	—

*Calculated data according to [101].

Sodium nitride. In contrast to lithium sodium interacts only with nitrogen, transferred to the atomic state by an electric discharge, by the irradiation of sodium vapors in a nitrogen atmosphere [15], or by the action of nitrogen on sodium hydride [9]. In both cases a nitride of the composition Na_3N is obtained.

The azide of sodium NaN_3 has been more studied, forming by only indirect means [15, 16]. The nitride NaN_3 is produced by passing notrous oxide over molten sodium amide

$$2\,NaNH_2 + N_2O \rightarrow NaN_3 + NaOH + NH_3.$$

This reaction, according to [9], occurs at a temperature of 100-160°C in the course of 9.5 h with a yield of about 90%. The NaN_3 will also be formed by the following reactions

$$NaNO_3 + 3\,NaNH_2 \rightarrow NaN_3 + 3\,NaOH + NH_3\ (175°C),$$
$$N_2H_4 \cdot H_2O + C_2H_5NO_2 + NaOH \rightarrow NaN_3 + C_2H_5OH + 3\,H_2O,$$
$$Na + NH_4N_3 + NH_{3(liquid)} \rightarrow NaN_3 + 2\,NH_3 + H.$$

Sodium nitride Na_3N is stable at room temperature, in air and in hydrogen it is decomposed by water; upon heating to 300°C it dissociates; it reacts readily with chlorine, phosphorus and sulfur. Dilute acids decompose the nitride with the formation of ammonia and the corresponding sodium salts.

Sodium azide NaN_3 is white nonhygroscopic substance; at room temperature it dissolves in water with the formation of an electric conducting solution (at 17°C in 100 parts H_2O 41.7 parts NaN_3 is dissolved) [15, 24]. At high temperatures NaN_3 is decomposed by water according to the scheme

$$3\,NaN_3 + 3\,H_2O \rightarrow 3\,NaOH + NH_3 + 4N_2.$$

It dissolves in nonaqueous solvents: gasoline, alcohol, benzene. In 100 parts of nonaqueous alcohol at 16°C 0.315 g of NaN_3 is dissolved, at 0°C – 0.22 g of NaN_3.

Upon heating to 270°C NaN_3 is decomposed without melting.

In work [22] the azide single crystals NaN_3 were studied. Single crystals with dimensions of 4 × 6 × 1 mm were produced in a

special convection tube. A study of the bands of double refraction of single crystals showed that they intersect at an angle of 120° and represent a plane in the crystal at a certain angle to axis c with an index (110). The appearnace of the planes is connected with the phenomena of slip, a combination of slip and twinning, multiple twinning.

Irradiation with γ-rays at a dose of 10^7 R causes the appearance of deep grooves along these lines of intersection, and also pyramidal etching pits.

A survey of the properties of sodium nitride and azide can also be seen in [1017].

Potassium nitrides. Analogous to sodium potassium does not interact with molecular nitrogen even under pressure or at high temperatures [15]. With the action on potassium of nitrogen, activated by an electric discharge, two compounds of potassium with nitrogen will be formed: the nitride K_3N and the azide KN_3, where the nitride will be formed in considerably smaller quantities than the azide [15].

The usual method of producing potassium nitride is by heating potassium hydride KH in a stream of nitrogen [6, 9], and also by heating of potassium azide in a vacuum [16].

Potassium azide KN_3 is produced by the effect of potassium on a solution of NH_4N_3 in liquid ammonia according to the reaction [17, 15]

$$K + NH_4N_3 \rightarrow KN_3 + NH_3 + 1/2H_2;$$

with the action of KNO_3 on liquid ammonia [18, 15]

$$KNO_3 + 2NH_3 \rightarrow KN_3 + 3H_2O;$$

by passing nitrous oxide at 270-280°C over potassium amide [19, 20, 15]

$$2KNH_2 + N_2O \rightarrow KN_3 + NH_3 + KOH.$$

In the latter case the azide KN_3 will be formed with a high yield.

The nitride K_3N will be formed from the elements by an exothermic reaction. Upon heating with nitrogen or mercuric oxide potassium nitride loses nitrogen and reacts with water to KOH and NH_3 [9]; upon heating with phosphorus and sulfur it yields potassium phosphides and sulfides [21, 9]. Upon interaction with dilute acids potassium nitride will form ammonia the corresponding potassium salt. Potassium nitride is an unstable connection and is separated in its pure form with great difficulty.

The nitride (azide) KN_3 consists of a brilliant colorless crystals of tetragonal structure. It readily dissolves in water [15, 24]:

t, °C	0	10.5	15.5	17	100
KN_3 (g per 100 g H_2O)	41.4	46.5	48.9	49.6	105.7

In water it hydrolyzes with the formation of caustic potassium and ammonia

$$KN_3 + H_2O \rightarrow KOH + NH_3.$$

In presence of platinum niello the potassium azide is decomposed by water according to the following scheme

$$3KN_3 + 3H_2O \rightarrow 3KOH + 4N_2 + NH_3.$$

Potassium axide dissolves well in liquid ammonia, methyl and ethyl alcohols (in 100 g of ethyl alcohol at 0°C 0.16 g of KN_3 is

dissolved); it is less soluble in benzene [15, 16].

A solution of potassium azide does not react with iodine, but in presence of small quantities of CS_2 (0.04-0.08 mole per 1 mole of KN_3) an energetic reaction occurs

$$2KN_3 + 2I_2 \rightarrow 2KI_2 + 3N_2.$$

In work [22] single-crystals of KN_3 with dimensions of 6 × 6 × × 3 mm were produced by the evaporation of a saturated aqueous solution in the course of several months. As also in crystals of NaN_3, double refraction bands were detected, intersecting at an angle 90° and corresponding to planes with the index (112). The causes of their formation, and also the results of variation under the effect of γ-rays were the same, as for single-crystals of NaN_3.

The azide KN_3 is an explosive; it decomposes upon being melted.

Rubidium nitride. In a rubidium-nitrogen system there are two compounds: Rb_3N and RbN_3. Rubidium nitride Rb_3N is obtained by heating the hydride RBH in a stream of nitrogen [6, 9], and also by decomposing the azide RbN_3 at a temperature of the order of 340°C [23].

The azide RbN_3 is obtained by interaction of ammonia with rubidium carbonate, or rubidium hydroxide or by the reaction between rubidium sulfate and barium azide BaN_6 [23].

Rubidium nitride Rb_3N is red in color, is stable at normal temperatures in air and in hydrogen; upon heating in a hydrogen medium it is changed to the hydride RbH; it readily reacts with chlorine, phosphorus and sulfur. Upon the interaction of RbN_3 with dilute acids the corresponding rubidium salt and ammonia will be formed [25].

The azide RbN_3 is readily soluble in water: at 16°C the solubility is 51.7%. The solubility in absolute alcohol is 0.182 g per 100 g of alcohol; it is insoluble in ether [24]. With heating it changes into Rb_3N, and upon heating in a vacuum it decomposes to a metal and nitrogen which is used to produce rubidium of high purity [23]. In contrast to lithium, sodium and potassium azides it is not explosive.

Cesium nitrides. Cesium nitride CsN is obtained by heating its hydride CsH in a stream of nitrogen or by careful heating of the azide CsN_3 (at 340°C). The azide CsN_3 will be formed by the action of ammonia on cesium carbonate [24]

$$Cs_2CO_3 + 2NH_3 \rightarrow 2CsN_3 + H_2O + CO_2$$

or by the interaction between cesium sulfate and barium azide BaN_6 [9, 23].

Cesium nitride CsN_3 is a powder, grayish-green in color; it is stable in dry air; in moist air it decomposes with the liberation of ammonia; it is very hygroscopic. Its solubility at 16°C is 307.4 g per 100 g of water and 1.037 g per 100 g of absolute alcchol; it is insoluble in ether [24]. In hydrogen at normal temperatures it is stable and upon heating it is converted to the hydride CsH. Rubidium nitride CsN_3 [sic] readily reacts with sulfur, phosphorus and chlorine; it interacts with dilute acids to form salts and ammonia [25].

Upon heating it decomposes to the nitride Cs_3N and nitrogen, upon being heated in a vacuum it loses nitrogen completely, being transformed into metallic cesium. The azide CsN_3, as well as the corresponding rubidium azide, to not explode.

The properties of the nitrides and azides of the alkali metals are given in Table 33; the thermodynamic characteristics are given in [1017].

2. Nitrides of the Metals of the Copper Subgroup

Copper nitrides. The phase diagrams of the metals of the copper subgroup with nitrogen have not been studied. Nitrogen does not dissolve either in solid or in liquid copper, at least up to temperatures of 1400°C, at which investigations have been conducted [26, 27]; interactions of copper with nitrogen have not been detected up to 900°C [28].

Nevertheless in the copper-nitrogen system the existence of the three compounds Cu_3N, CuN_3 and $Cu(N_3)_2$ have been detected, obtained by indirect methods.

The nitride Cu_3N is obtained by passing ammonia over finely pulverized CuO, Cu_2O or CuF_2 at a temperature of 250-280°C [29]. The assumptions about the formation of copper nitrides with the passage of ammonia over copper temperatures of 900-1000°C have not been confirmed. The fragility of copper under these conditions is explained not by the formation of chemical compounds, but by the effect on copper of hydrogen, obtained by the dissociation of ammonia.

The Cu_3N will also be formed by the action of ammonia on copper hydroxide [1]

$$6NH_3 + 3(4CuO \cdot H_2O) = 2Cu_3N + 3Cu_2O + 2N_2 + 12H_2O.$$

Copper azide CuN_3 is produced by the reduction of copper sulfate with the help of $KHSO_3$ by the addition of sodium azide [30].

Copper nitride Cu_3N is a dark-green powder, stable in air under normal conditions, but decomposing upon heating in a vacuum to 450°C. The Cu_3N has a cubic structure of the ReO_3 type, the space group $Pm3m(O'h)$ with one formula unit in the unit cell [31, 32]. Copper nitride Cu_3N is a semiconductor with an electric resistance of $6 \cdot 10^2$ $\Omega \cdot cm$ at room temperature and with a width of the forbidden zone of 0.23 eV [33]. The temperature dependence of the electric resistance of Cu_3N is shown in Fig. 33.

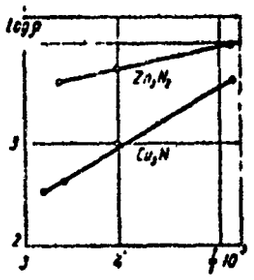


Fig. 33. The temperature dependence of the electric resistance of Zn_3N_2 and Cu_3N.

It is readily dissolved in acids; upon dissolution in HCl cuprous chloride and ammonium chloride will be formed [34]; it is violently decomposed in concentrated H_2SO_4 and HNO_3. At 400°C in a stream of oxygen it is oxidized with intense heating; it is decomposed in a vacuum at 450°C [24].

Copper azide CuN_3 is an unstable compound, forming with a great increase in free energy ΔE^0, the component according to [35], for the reaction Cu + 3/2 N_2 = CuN_3 71219 cal. The azide CuN_3 has a tetragonal crystalline structure; space group C_4^6h with eight formula units in the unit cell [30]. The structure consists of copper ions and linear groups of nitrogen atoms (N_1 is in the middle, N_2 is on the outside), which are located in the form of chains in direction (111). The shortest intervals are Cu-Cu = = N_1-N_1 = 3.36; Cu-N_1 = 2.795; Cu-N_2 = 2.23; 3.28 and 3.56; N-N_2 = 3.56 Å.

Earlier the structure of CuN_3 was considered rhombohedral [36].

The authors [24] indicate the existence of another azide of bivalent copper $Cu(N_3)_2$, which is obtained by the reaction

$$Cu(NO_3)_2 + 2NaN_3 = Cu(N_3)_2 + 2NaNO_3$$

or upon the interaction of those same reagents in the hydrated state in an alcohol solution or by the decomposition of the compound $Cu(N_3)_2 \cdot 2NH_3$ [37]. The azide depending upon the method of production has the form of a black-brown powder or opaque needles of the same

color (it is crystallized in a rhombic system). It is poorly soluble in water and in organic solvents; it is readily soluble in acids, CH_3COOH and NH_4OH; in an aqueous solution of hydrazine it is reduced to CuN_3. It readily explodes; it is distinguished by intense detonational properties, detonating 6 times more powerfully than lead azide and in 450 times more powerfully than fulminating mercury [24].

Silver nitrides. Nitrogen does not dissolve either in solid or in liquid silver up to 1300°C, however by indirect methods silver nitride Ag_3N and silver azide AgN_3 are produced [26].

Siler nitride Ag_3N will be formed during the prolonged storage ammonium solutions of silver oxide or by the decomposition of an ammonium solution of Ag_2O by alcohol, and also by acetone and by the precipitation of an ammonium solution of AgCl by a solid alkali [39]. Upon the dissolution of Ag_2O in a concentrated ammonia solution and subsequent setting preparations of Ag_3N are obtained, contaminated with an admixture of silver and Ag_2O. Preparations of Ag_3N contaminated with silver will also be formed and with the holding of $Ag_2N \cdot 2NH_3$ compound over sulfuric acid [24]. Silver nitrides can also be produced by the interaction of silver vapors with ammonia at 1280°C [6].

The silver azide AgN_3 is obtained by the interaction of silver nitrate with hydrazine sulfate or hydrazoic acid [1, 9] or by the interaction of silver nitrate with sodium azide [24]

$$AgNO_3 + NaN_3 =$$
$$= AgN_3 + NaNO_3.$$

The nitride Ag_3N has the form of black flakes or black brilliant crystals; it is insoluble in water, soluble in the dilute mineral acids; it reacts explosively with concentrated acids [24]; in air in the dry and humid state it is stable; it slowly decomposes at room temperature. It is resistant in cold to the effect of

alkalis; in a vacuum at room temperature it rapidly decomposes [39]. An important peculiarity of Ag_3N is its capacity to explode (Berthollet's fulminating silver); it decomposes explosively in air at 165°C, and also in contact with various solids, with friction or shock.

Silver nitride Ag_3N has a face-centered cubic lattice, in which the nitrogen atoms occupy octahedral pores in FCC-lattice of silver atoms [39].

Silver azide AgN_3 is a colorless substance, crystallized in the form of needles (a rhombic pseudotetragonal lattice, a rhombically distorted KN_3 type); upon heating to a temperature of 170-180°C the color changes to grayish-violet. It is readily soluble in an aqueous solution of ammonia, and in potassium cyanide; it is not very soluble in water (0.01 weight parts per 100 weight parts of water) and nitric acid. It is an explosive, which is exploded by by shocks, and also upon heating to approximately 300°C.

Gold nitrides. Nitrogen does not dissolve in solid and liquid gold up to a temperature of 1300°C [26]. Two gold nitrides are known. One of them - the hydrate-nitride $Au_3N \cdot 5H_2O$ - is obtained by the action of ammonia on gold oxide with subsequent boiling of the formed product in water. With the interaction of AuO with ammonia the nitride of bivalent gold Au_3N_2 will be formed [1, 9]

$$3AuO + 2NH_3 = Au_3N_2 + 3H_2O.$$

Both nitrides are explosives. In Table 35 the basic properties of the metals of the copper subgroup.

Table 35. Properties of nitrides and azides of the metals of the copper subgroup.

Characteristic	Cu_3N	CuN_3	$Cu(N_3)_2$	Ag_3N	AgN_3	Au_3N_3
Nitrogen content, wt. %	6,84	89,81	43,03	4,15	28,03	4,53
Crystal structure	Cubic [32]	Tetragonal [30]	Rhombic [24]	Face-centered cubic [39]	Rhombic	—
Lattice constants, Å:						
a	3,807	8,65$_3$ [30]	—	4,369 [39]	5,58 кХ	—
b	—	—	—	—	5,93	—
c	—	5,59$_4$	—	—	6,04	—
c/a	—	0,646	—	—	—	—
Specific weight	5,84	3,34	—	9,0 [39]	—	—
Melting point, °C	—	—	—	—	252	—
Decomposition, temp., °C	—	—	—	—	300	—
Heat formation, kcal/mole	—17,8	—60,23 [35]	—	—61,0 [39]	—67,3 [40]	—
Entropy, cal/mole·deg	—	39,68 [35]	—	—	—	—
Heat capacity, cal/mole·deg	21,7 [38,273—373]	—	—	—	—	—
Specific electric resistance, Ω·cm	$6,0 \cdot 10^2$ [33] (20°C)	—	—	—	—	—

C H A P T E R IV

METAL NITRIDES OF GROUP II OF THE PERIODIC SYSTEM

1. Beryllium, Magnesium and the Alkaline-Earth Metal Nitrides

Beryllium nitrides. The Be-N_2 system has not been investigated; only the existence in it of the nitride Be_3N_2 and the azide $Be(N_3)_2$ has been established. The nitride Be_3N_2 is obtained by the interaction of powdery beryllium with nitrogen at a temperature of 500°C and at 900°C in the case of the use of lumpy beryllium [6]. The formation reaction of the nitride occurs slowly (from 24 to 60 h); to accelerate hydrogen (2-6%) is added to the nitrogen which is a catalyst of this reaction.

The kinetics of the interaction reaction of beryllium with nitrogen were investigated in the works of Gulbransen and Andrew [41], who established that the rate of the reaction at temperatures of up to 850°C was slow, at 950°C the reaction occurs two times slower than the oxidation reaction of beryllium. As a result of the conducted experiments [41] on nitridation at 76 mm Hg within the limits of 725-925°C the parabolic law of nitridation was detected with an activation energy of Be_3N_2 of 75000 cal/mole. Upon nitridation of beryllium very dense, gas-impermeable films will be formed, intensely hampering of the nitridation process [76].

According to [42], the nitridation of pig beryllium with the passage of 64-fold amount of nitrogen changes at 700°C to 56%, at 800°C - to 70%, and at 900°C it is almost completely terminated even

in the absence of hydrogen. By the nitridation of beryllium powder at 1000°C in the course of 12-18 h with a mixture of nitrogen with 5% hydrogen beryllium nitride powder was produced, containing 95-98% Be_3N_2, 1-5% BeO and 0.05-0.2% Be_2C [42].

Beryllium nitride can be produced by the nitridation of the metal with ammonia: from technical finely pulverized beryllium after nitridation in a current of dry NH_3 in the course of 3 h at 850°C and the subsequent three-fold nitridation at 1000°C products are produced, containing 94-95% Be_3N_2. With the use of purer metal there can also be produced by this method purer nitride [24]. An analogous method of obtaining beryllium nitride by the nitridation of the metal powder with ammonia at a temperature of 1000°C was described by Busev [6].

Chiotti [43] by nitriding beryllium powder with ammonia in the course of 5 h at 800°C and 17 h at 900°C obtained products, containing respectively 46.4 and 43.2% nitrogen (as compared to 50.89% nitrogen in Be_3N_2). After treating these products in a vacuum at 2000°C X-ray-diffraction analytically pure beryllium nitride was obtained.

A promising method of obtaining beryllium nitride of technical purity is the reduction beryllium oxide by carbon in a stream of nitrogen [9], and also the heating of beryllium carbide Be_2C in a stream of nitrogen at 1250°C or in stream of ammonia at 1000°C [42].

Beryllium azide $Be(N_3)_2$ is obtained by heating the compound $Be(CH_3)_2$, frozen at the temperature of liquid nitrogen with a surplus of ether solution of HN_3, however it is very difficult to separate it from the aqueous solutions due to the tendency to hydrolyze.

The solubility of nitrogen in beryllium is small [44].

Beryllium nitride Be_3N_2 is in its pure state a white substance,

in its contaminated state - gray-colored powder. It crystallizes to a cubic system of the anti-Mn_2O_3 type; it melts at a temperature of 2200°C; it decomposes with the liberation of nitrogen at temperatures higher than 2240°C (the elasticity of dissociation attains 1 at at 2400°C), in a vacuum it sublimates at 2000°C [45].

According to [961], beryllium nitride vaporizes at temperatures of 1640-1950°K congruently, its decomposition according to the reaction Be_3N_2 (solid) = 3Be (gas) + N_2 (gas) occurs simultaneously; the pressure of nitrogen (at) is determined by the equation

$$\lg p_{N_2} = -1{,}898 \cdot 10^4 T^{-1} + 6{,}213.$$

The enthalpy of dissociation is equal to -136 ± 5 kcal/mole, which agrees well with the data accepted in literature (-137.8 ± ± 1.5 kcal/mole). Langmuir enthalpy of activation for samples with a porosity close to 18% is equal to 430.2 ± 6.8 kcal/mole, which is 22% higher than equilibrium enthalpy. The vaporization coefficient of Be_3N_2 is equal to 0.001. Beryllium nitride possesses great hardness; in the presence of additives of Al_2O_3 and certain others it acquires the ability to phosphoresce [6].

The heat capacity of Be_3N_2 is expressed by the series C_p = = 15.45 + $19.64 \cdot 10^3 T - 4.80 \cdot 10^5 T^{-3}$ cal/deg·mole [47].

Beryllium nitride is completely stable in air; it is very slowly decomposed by boiling water with the liberation of ammonia; it is decomposed by dilute by solutions of halide acids with the formation of halide salts of beryllium; concentrated HCl interacts with Be_3N_2 at a temperature of 700-800°C with the formation of anhydrous $BeCl_2$

$$Be_3N_2 + 8HCl = 3BeCl_2 + 2NH_4Cl.$$

With boiling with oxygen-containing acids it is slowly decomposed. At temperatures up to 500°C Be_3N_2 is resistant to oxidation with dry oxygen; at a temperature of 1000°C it is rapidly oxidized [42, 45].

Beryllium azide rapidly decomposes in humid air; in a flame it bursts into flame; it does not detonate [44, 9].

Articles of beryllium nitride are prepared by sintering, by hot pressing in graphite molds at a temperature of 1800-1900°C, at a pressure of 140 kg/cm^2 with the production of a density, close to theoretical [42].

The addition beryllium nitride to beryllium leads to a reduction in the plasticity of beryllium, and to an increase in its strength at increased temperatures (Table 36).

Table 36. The effect of Be_3N_2 additives on the mechanical properties of beryllium [42].

Be_3N_2 additive, %	Tensile strength, kg/mm^2		Relative elongation, %	
	600°C	800°C	600°C	800°C
0	14,3	4,4	18,2	6,6
5	17,5	—	3,4	—
10	~14—15	—	~2,3	—
20	~14—15	6,1	~2,3	6,4

Magnesium nitride. In a magnesium-nitrogen system the existence of the nitride Mg_3N_2 and the azide $Mg(N_3)_2$ has been established, where Mg_3N_2 exists in one crystal form [1025]. The formation of magnesium nitride was detected by St. Claire Deville and Caron [48] upon the sublimation of magnesium in air. Magnesium nitride will be formed in the shape colorless, needle-shaped crystals which are rapidly decomposed by water with the formation of magnesium oxide

and the liberation of ammonia. The first systematic investigation of the process of the formation of magnesium nitride was conducted by Brigleb [49] by heating magnesium filings in a stream of ammonia or nitrogen in porcelain combustion boats. It was noticed that silicon passes into the composition of the nitride from the boat, therefore it is recommended that boats, already previously in use, be used for the production of the nitride. In this same work magnesium nitride, contaminated with silicon, was obtained by the heating of magnesium silicide in a stream of nitrogen.

Hartung [50] produced magnesium nitride by heating of magnesium powder in an ammonia medium and established that the interaction reaction between the magnesium and the nitrogen begins at a temperature of 450°C, and occurs most intensively at 600-700°C; at 900°C the formed nitride dissociates.

Murgulescu and Cismaru [244] demonstrated that at 500-580°C magnesium is nitrided by nitrogen at atmospheric pressure. The temperature dependence of rate of the reaction has a parabolic character, and the activation energy of the process is 31.7 kcal/mole.

Merz [51] found that magnesium nitride is readily produced by the simple heating of magnesium in a glass test tube in the air in the flame of a gas burner. Moreover, as also in experiments [49], the transfer of silicon from the glass into the composition of the nitride was detected, accompanied by turbidity and blackening of the glass.

Kaiser [52] produced magnesium nitride by the action of nitrogen on heated magnesium sulfide and chloride, and also on magnesium hydride, and it was revealed that magneisum hydride readily converts to nitride, and the latter - back in hydride

$$3MgH_2 + 2N_2 = Mg_3N_2 + 2NH_3,$$
$$2Mg_3N_2 + 12H_2 = 6MgH_2 + 4NH_3.$$

In the opinion of Smits and Paschkovetsky [53, 54], for the preparation of magnesium nitride it is better to use not nitrogen, but ammonia. The passage of dry ammonia over magnesium, heated to 600°C, produced Mg_3N_2 also in [6]. Conversely, Neumann with his colleagues [55] holds the opinion that in the nitridation of magnesium by ammonia an intense adsorption of ammonia by the nitride occurs which delays dissociation and participation in the process of nitride-formation.

Kirchner [56] obtain surface layers of magnesium nitride on compact magnesium samples upon heating them in air.

According to Eidmann and Moser [57], magnesium nitride can be produced by heating magnesium powder mixed with highly oxidizing metals in air, and also in mixture with carbides of certain metals. For example, a mixture of equal parts of magnesium and iron, heated in an open crucible, will form a product, containing about 36% magnesium nitride. According to the same data, upon heating magnesium powder in a tightly closed crucible with a very small hole in the cover two layers will be formed: an upper layer - of magnesium oxide and a lower one - of nitride. Eidmann [58] observed the formation of magnesium nitride with the heating to red heat of metallic magnesium powder with boron and silicon nitrides, and alkali and alkaline-earth metal cyanides.

Szarwasy [59] obtained magnesium nitride by heating of a mixture of magnesium filings with carbon first in a hydrogen medium and then in air.

Mehner [60] and Neuberger [61] prepared magnesium nitride by an analogous method: by heating a mixture of magnesium and carbon black in nitrogen medium.

Vocurnasos [62] discovered that magnesium nitride can be produced by the interaction of magnesium with cyanides, where a reaction of the following type

$$2KCN + 3Mg = Mg_3N_2 + 2K + 2C$$

takes place very energetically.

Of all the enumerated, and frequently very ingenious methods of obtaining magnesium nitride only those methods have practical application, which are based on the treatment of heated magnesium with nitrogen or ammonia. However up till now the optimum temperature conditions of carrying out these processes have not been worked out.

The majority of researchers propose relatively high temperatures for the nitridation of magnesium: within the limits of from 700 to 900-950°C. Thus, according to Zhukov [63], the interaction of magnesium with nitrogen with the formation of nitride begins at 780-800°C; according to Neumann, Kröger and Kun [64] it is recommended that magnesium nitride be produced by the nitridation of magnesium powder, freed of iron by magnetic separation, in a current of dexoygenated nitrogen during the course of 4-5 h at a temperature of 800-850°C (the nitrogen content in such a nitride is 27.3-27.6% which almost corresponds exactly to the calculated content of nitrogen in Mg_3N_2, equal to 27.74%). Porter [65] indicates that the nitridation of magnesium by ammonia, preheated to 300°C, or by nitrogen, heated to 400°C, should be carried out at 900-1000°C. Davis [66] for the production of magnesium nitride in a stream of nitrogen or ammonia recommends using a temperature, located within the limits between the sublimation and boiling points of magnesium so the the sublimated magnesium could destroy the nitride layer for the purpose of continuous nitridation. Stackelberg and Paulus [46] produced magnesium nitride by heating magnesium for 4 h in a stream of ammonia at a temperature of 850°C with subsequent 1.5 h of heating in a stream of nitrogen to remove the adsorbed ammonia. In this same work a method of preparing single-crystals of magnesium nitride is described, consisting of the rapid heating of a piece of magnesium up to 1050°C (i.e., almost to the melting point, equal to 1107°C) in a slow stream of nitrogen in an iron combustion boat. On the surface

of the piece of metal and on the walls of the boat transparent colorless needles of magnesium nitride crystals will be formed having a habit of nexahedral prisms with a trihedral pyramid or plane at the free end. The direction of needles is (111), of the lateral faces (211), of the pyramid or end site (111).

Mitchell [68] obtained rather pure magnesium nitride (with 0.9% MgO impurity) by passing nitrogen over magnesium filings in an iron combustion boat first at 650-700°C for 3-4 h, with a subsequent increase in temperature to 950°C and holding at this temperature for 12 h.

Murgulescu and Cismaru [244] demonstrated that at temperatures of 500-580°C magnesium is nitrided by nitrogen at atmospheric pressure. The rate of reaction obeys to the parabolic law; the activation energy is equal to approximately 31,700 cal/mole.

The authors [244] investigated the nitridation of compact magnesium at a pressure of nitrogen fom 7.5 to 30 at, at temperatures from 575 to 635°C for a long period of time (more than 115 h). In this work, as in [271], it was shown that nitridation with the surface occurs slowly; magnesium nitride will be formed, close in composition to stoichiometric magnesium nitride.

The experiments on producing magnesium nitride were repeated by us jointly with T. V. Dubovik and V. S. Polishchuk [242]. Magnesium filings with dimensions of 0.1-0.2 mm were nitrided in a porcelain boat, located in a reactor and surrounded by nitrogen. As the obtained data showed (Fig. 34), noticeable absorption of nitrogen by the magnesium begins at a temperature of 500-550°C, ending with the formation of a nitride (with a nitrogen content of 26.5%) after 4 h at 800°C and 1/2 h at 900°C. The magnitude of the lattice constant of magnesium nitride was found to be a = 9.92 Å which coincides well with the tabular data for Mg_3N_2.

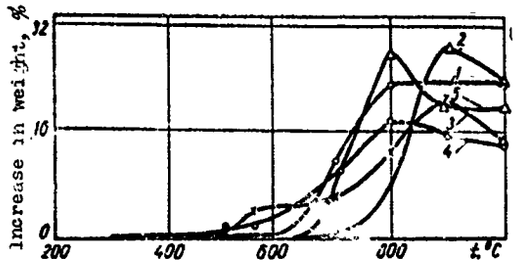


Fig. 34. The dependence of the degree of nitridation of magnesium on temperature and time: 1 - 15; 2 - 30; 3 - 60; 4 - 120; 5 - 240; min.

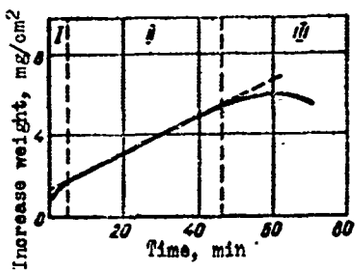
An analysis of the mechanism of the process of nitridation of magnesium leads to the following conclusions. The sharp acceleration in nitridation process at 700°C can be explained in accordance with the data of work [75], according to which, in spite of the relatively low activation energy with the nitridation of magnesium, the diffusion of nitrogen into the magnesium occurs slowly (approximately two times slower than oxidation, although the activation energy of oxidation is almost two times greater than the activation energy of the nitridation of magnesium). This is explained by the formation on the magnesium of a dense gas-impermeable film. Obviously, up to a temperature of 700°C the film substantially impedes the nitridation process. At 700°C the melting of the magnesium occurs and the breakdown of the integrity of the film and the nitridation process is sharply accelerated. Nitridation at a temperature of 900-1000°C actually occurs even with melted magnesium, the nitridation surface of which is limited by the surface of the molten metal. Therefore nitridation in general proceeds more poorly. At a temperature of 800°C it is still not possible to form a surface of molten magnesium and the nitride film has already been destroyed, consequently, 750-800°C can be considered the optimum temperature for the nitridation process.

The indicated peculiarities of the process of the formation of magnesium nitride lead to the conclusion of necessity of introducing into the magnesium powder before nitridation of a sufficiently inert filler, which would prevent the sintering the magnesium powder and the formation on it of a continuous nitride film. As such a filler previously obtained magnesium nitride has been used [242]: for the normal course of the process the amount of nitride should be 30-40%.

This method makes it possible to obtain a nitride of sufficiently high quality composition.

The kinetics of the nitridation of magnesium were studied in detail in [75]. They used pure magnesium, containing 0.01% Fe, 0.005% Mn, 0.005% Al, 0.001% Si, 0.0001% Cu, 0.005% Pb, and nitrogen, thoroughly purified by passing it over copper shavings at 400°C through a column with $Mg(ClO_4)_2$ for the removal of O_2 and H_2O. Figure 35 shows the isothermal curve of magnesium nitridation, which has three sections: the first section, the nitridation section and the section, at which the vaporization of magnesium begins to intensively take affect. The effect of the temperature of nitridation within limits of 415-485°C in Fig. 36, from the data of which the equation of the temperature dependence of the nitridation constant was derived.

$$K = 2{,}2 \cdot 10^4 \exp(22300/RT)\ [\text{mg/cm}^2 \cdot \text{h}].$$



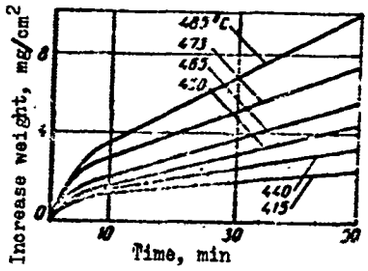


Fig. 35. Fig. 36.

Fig. 35. Nitridation of magnesium at 465°C (p_{N_2} = 100 mm Hg): I - the initial period of nitridation; II - the period of nitridation; III - the period of vaporization.

Fig. 36. The temperature dependence of the nitridation of magnesium (p_{N_2} = 100 mm Hg).

A comparison with the constant of the oxidation rate of magnesium $K = 6.2 \cdot 10^{12} \exp(50500/RT)$ shows that the activation energy of the

nitridation process is two times less than activation energy of the oxidation process (Fig. 37). However the nitridation rate is many times less than the oxidation rate which is explained (within the limits of the second kinetic section of the nitridation process) by the formation of a dense, gas-impermeable film of nitride on the magnesium. The increase in the nitridation pressure causes an increase in the constant of the nitridation speed (Fig. 38).

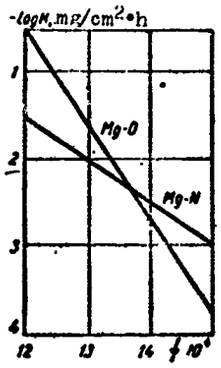


Fig. 37.

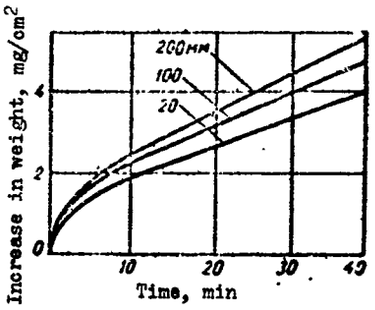


Fig. 38.

Fig. 37. The temperature dependence of the reaction constants of the oxidation and the nitridation of magnesium.

Fig. 38. The dependence of the rate of nitridation of magnesium on pressure at a temperature of 465°C.

A comparison of the kinetics of the nitridation and oxidation of magnesium was also made in [272]. It was demonstrated that the differences in the processes are connected with the fact that crack formation in the oxidized layer occurs more readily than in the nitrided layer. And with oxidation, and with nitridation at first a layer stable in time will be formed, the subsequent increase in which to a certain critical thickness causes the appearance of cracks.

In work [247] the kinetics of the nitridation fine magnesium powders of brands M-3 (99.57% Mg) and M-4 (99.60% Mg) with an admixture of iron (0.01-0.023%) was also studied. The dimensions of the M-3 powder particles were on the average 250-300 μ, and M-4 – about 50-100 μ. It was determined that at 400°C in both cases the

time dependence of nitridation obeys the logarithmic law, and at 450°C – the parabolic law. The kinetic characteristics of the process of the nitridation of magnesium powders are given in Table 37.

Table 37 The kinetic characteristics of the process of nitridation of magnesium powders.

Make of powder	Temperature, °C	Equation of rate of nitridation	Constant reaction rate K, mg/cm⁴·h	Activation energy, kcal/mole
M-3	400	$\Delta m^* = 0{,}0056\ lg\tau^{**}$	0,0056	49,97
	450	$\Delta m = -0{,}0315 + 0{,}0733\tau - 0{,}00932\tau^2$	0,07425	
M-4	400	$\Delta m = 0{,}00165\ lg\tau$	0,00165	42,54
	450	$\Delta m = 0{,}00664 + 0{,}0021\tau + 0{,}000355\tau^2$	0,01485	

* Δm – the increase in weight mg/s².
** τ – the time of nitridation, h.

It is noted that the course of the nitridation process on damping curves is caused by the protective properties of the magnesium nitride film. Powder M-4 is more reactive than M-3, due to the magnesium. Powder M-4 is more reactive than M-3 due to the very well-developed surface (the specific surface of M-4 is equal to 3500, and M-3 – to 616 cm^2/g); this, in particular, is attested to by the lower activation energy of the nitridation of powder M-4.

The experiments conducted in this work on the oxidation of magnesium powders in air showed that MgO and Mg_3N_2 will be formed simultaneously.

According to [246], the nitridation of magnesium is substantially accelerated by the addition to it as a catalyst of 5% KHF_2.

The magnesium azide $Mg(N_3)_2$ is produced by dissolution of magnesium of hydrazoic acid [1, 9].

Magnesium nitride Mg_3N_2 is a friable powder of yellow-orange color, intensely fluorescing when irradiated with ultraviolet rays [68]. The Mg_3N_2 has a cubic face-centered lattice, analogous to

the lattices of magnesium stibnide and bismuthide, and also of beryllium nitride, with a constant, composing according to various data from 9.93 to 9.95 Å. In the nitride unit cell there are 16 formula units. According to Mitchell [68], magnesium nitride exists in three allotropic versions α, β and γ; the temperature of the α ⇄ β-transformation is 823°K (the heat of transformation is 220 cal/mole), and the temperature of the β ⇄ γ-transformation is 1061°K (the heat of transformation is 260 cal/mole).

The variation in the heat content of the individual versions within the limits of from 350 to 1200°K is determined by the equations

$$\Delta H_\alpha = -7125 + 22{,}81T + 3{,}65 \cdot 10^{-3}T^2,$$
$$\Delta H_\beta = -10020 + 29{,}60T,$$
$$\Delta H_\gamma = -9695 + 29{,}54T.$$

According to Kelley [38], the molar heat capacity of the different versions of the nitride Mg_3N_2 can be calculated from the equations

$$C_{p\alpha} = 20{,}77 + 11{,}20 \cdot 10^{-3}T \quad (298 - 823\ \text{K}),$$
$$C_{p\beta} = 20{,}07 + 10{,}66 \cdot 10^{-3}T \quad (823 - 1061^\circ\text{K}),$$
$$C_{p\gamma} = 28{,}50 \quad (1061 - 1300^\circ\text{K}).$$

The specific electric resistance of the nitride is equal to $2 \cdot 10^6$ Ω·cm [63].

Magnesium nitride is stable in dry air; the temperature of dissociation under these conditions is equal to 1500°C [1]. In humid air the nitride is rapidly decomposed with the liberation of ammonia [69, 24]

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3,$$

thus storing it is possible only in sealed ampules [64].

Whitehouse [70] found that magnesium nitride is reduced by water gas to metallic magnesium with the simultaneous formation of carbon and cyanamides; dry hydrogen does not reduce the nitride to metallic magnesium.

In dry oxygen magnesium nitride burns with intense incandescence and radiation of light. With concentrated and dilute acids and phosphorus trichloride it reacts according to the following patterns:

$$Mg_3N_2 + 8HCl = 3MgCl_2 + 2NH_4Cl,$$
$$Mg_3N_2 + 8HNO_3 = 3Mg(NO_3)_2 + 2NH_4NO_3,$$
$$5Mg_3N_2 + 6PCl_5 = 15MgCl_2 + 2P_3N_5.$$

Magnesium nitride does not react with ethyl alcohol, an alcohol solution of glycerine, oxalic acid and phenol [71].

The interaction of magnesium nitride with carbon monoxide and carbon dioxide was studied by Fichte and Scholig [72], who established that at a temperature of 1000-1250°C these reactions are described by the following equations:

$$Mg_3N_2 + 3CO = 3MgO + 3C + N_2,$$
$$2Mg_3N_2 + 3CO_2 = 6MgO + 3C + 2N_2,$$

where the interaction reaction of magnesium nitride with CO_2 proceeds more actively than with CO.

The magnesium azide $Mg(N_3)_2$ upon heating decomposes explosively [1].

The physical properties of magnesium nitride Mg_3N_2 are given in Table 38. At the present time the semiconductor properties of magnesium nitride are being investigated, however its practical use in this region is very problematical due to its low chemical stability.

Table 38. The properties of the alkaline-earth metal nitrides.

Characteristic	Be_3N_2	Mg_3N_2	α-Ca_3N_2	β-Ca_3N_2	γ-Ca_3N_2	CaN_2	Sr_2N	Sr_3N_2	Sr_5N_4	SrN_2 · $Sr(N_3)_2$	Ba_2N	Ba_3N_2	BaN_2	BaN_6 — $Ba(N_3)_2$
Nitrogen content, weight, %	50,89	27,24	18,9	18,9	18,9	67,69	7,40	9,64	17,57	48,93	4,85	9,25	16,94	38,12
Crystal structure	Cubic	Face-centered cubic	Pseudo-tetragonal	Cubic of anti-Mn_2O_3 type [80]	Rhombic [270]	—	—	Pseudo-tetragonal [76]	—	Rhombic	—	Pseudo-hexagonal [46]	—	Monoclinic [88]
Lattice constant, Å														
a	8,15[46]	9,93[46]	3,56 [80]	11,42 [80]	—	—	—	—	—	11,82 [36]	—	—	—	6,22 kX [89]
b	—	—	—	—	—	—	—	—	—	11,47	—	—	—	22,90 kX
c	—	—	4,12	—	—	—	—	—	—	6,08	—	—	—	7,02 kX
c/a	—	—	1,157	—	—	—	—	—	—	—	—	—	—	105°14
Specific weight	2,72	2,74 [24]	2,67 [270]	2,64 [270]	2,63 [264, 265]	—	—	—	—	—	—	—	—	2.935 [9]
Melting point, °C	2200	—	—	1195		—	—	1027	—	—	—	1000	—	—
Decomposition point, °C	2240	—	—	1250 [63]	—	—	—	400—500 10^{-2} mm Hg	—	169 [1]	—	400—500 (10^{-2} mm Hg)	—	219—226 [1, 9]
Temperature of dissociation in °C at a pressure, mm Hg:														
1	—	1602	—	—	—	—	—	—	—	—	—	—	—	—
10^{-1}	—	1472	—	—	—	—	—	—	—	—	—	—	—	—
10^{-2}	—	1359	—	—	—	—	—	—	—	—	—	—	—	—
10^{-3}	—	1260	—	—	—	—	—	—	—	—	—	—	—	—
760	2400	—	—	—	—									
Heat of formation, kcal/mole	134,7± 1,5	110,24 [68]	105,0± 3,0 [76]	—	—	—75,8 [9]	—	92,2 [84]	—	—49,0 [84]	53,4±2 [81]	89,9 [9]	—	43,6 [86]
Entropy, kcal/g·deg	40,6	47,2	25,4 [76]	—	—	—	—	—	—	—	—	—	—	—
Specific electric resistance, Ω·cm	—	$2 \cdot 10^8$ [63] (298° K)	—	—	—	—	—	—	—	[81] 100	—	—	—	—

More practicable is the application of magnesium nitride as a dehydrating agent in inorganic and organic synthesis and in the rubber industry [65]. The negative effect of the formation of magnesium nitride in magnesium alloys is well known [73], where it increases the porosity and sharply reduces the mechanical properties, especially the resilience, both at room temperature and also at high temperatures; however a noticeable effect on the workability of alloys by pressure and their aging processes has not been found.

Calcium nitrides. The section of the phase diagram of the calcium-nitrogen system in the region of alloys, rich in calcium, is shown in Fig. 39 [77].

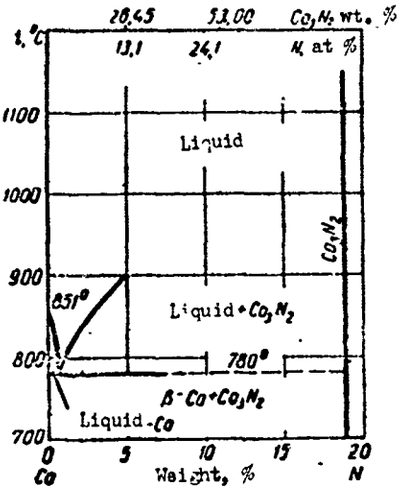


Fig. 39. A section of a phase diagram of Ca-N system.

In the calcium-nitrogen system the presence of three compounds has been established – Ca_3N_2, Ca_3N_4 and CaN_6.

The Ca_3N_2 exists in three versions: α, β and γ [1025, 1072].

The low-temperature version, black in color, β-Ca_3N_2 is formed at a temperature higher than 350°C by the interaction of nitrogen and ammonia with metallic calcium, changes at a temperature of 700°C into α-Ca_3N_2, where the transition is possible only in one β → α direction [263]. The interaction of calcium with nitrogen already

begins at room temperature, and upon heating the reaction proceeds very rapidly and explosively. The normal temperature for obtaining β-Ca_3N_2 is 450°C, at which the calcium is held in a stream of purified nitrogen for a period of 3-4 h [24]. The presence of oxygen in the calcium sharply inhibits the nitridation process and increases the temperature of the beginning of nitridation due to the poor gas-permeability of the calcium oxide film. Conversely, the presence of even a small admixture of sodium assists nitridation, since the sodim prevents the formation on the calcium of a continuous nitride film. In the nitridation of calcium by ammonia along with the nitride there is also obtained a certain amount of calcium hydride.

It was found that β-Ca_3N_2 has a pseudohexagonal structure; the density is 2.67 g/cm^3.

The average-temperature brown modification α-Ca_3N_2, existing in a temperature interval of 700-1050°C, has a cubic lattice of the anti-Mn_2O_3 type; its density is 2.64 g/cm^3 [1072].

The existence of the high-temperature yellow version γ-Ca_3N_2 was first indicated by Moissan [264, 265], then confirmed by other authors [77, 266, 268, 269]; it was investigated in detail in [270]. The γ-Ca_3N_2 phase has a rhombic structure; its density is 2.63 g/cm^3. It is formed by the nitridation of calcium at temperatures higher than 1050°C with subsequent rapid cooling, i.e., by condensation from the vapor phase. The formation of γ-Ca_3N_2 proceeds especially intensively with the introduction of heated calcium into nitrogen at 1200-1300°C and with rapid (practically instantaneous) cooling. Good results are given by the nitridation of calcium in a boat of fired Al_2O_3; the carrying out of the process in boats of other materials causes the formation of by-products (in iron and steel - calcium cyanamide, and in boats of silica - calcium silicate). Upon heating to 900°C the sudden transition of γ-Ca_3N_2 to α-Ca_3N_2 occurs. This transition, as well as the transition $\beta \rightarrow \alpha$, is possible only in one direction, i.e., $\gamma \rightarrow \alpha$.

Calcium nitride is stable upon heating and melts without decomposition at a temperature of 1195°C. It is obvious, that this pertains to γ-Ca_3N_2 or most likely to a mixture of the α- and γ-phases, which were most frequently produced in early operations by the nitridation of calcium (for example, to the high-temperature product of nitridation, having a yellowish-golden color; a cubic lattice of the anti-Mn_2O_3 type was assigned [29]). Zhukov [63] assumed that the upper boundary of temperature stability of calcium nitride was a temperature of 1250°C.

The molar heat capacity of calcium nitride (β-Ca_3N_2), according to Kelley [38], in the interval 298-800°K is expressed by the temperature dependence $C_p = 20.44 + 22.0 \cdot 10^{-3}$ T cal/mole·deg; a somewhat different expression is given in [76].

Calcium nitride is decomposed by water with the formation of $Ca(OH)_2$ and ammonia; it is also decomposed by weak mineral acids; it is insoluble in alcohol.

According to [241], the solubility of calcium nitride Ca_3N_2 in LiCl varies within the temperature limits of 625-720°C from 0.068 to 0.085 moles of nitride per 1 mole of molten LiCl, which is substantially less than the solubility of lithium nitride in molten salts (see page 22).

The nitride Ca_3N_4 (pernitride) is obtained by heating calcium amide in a vacuum [6], and the compound CaN_6 - an azide, is obtained only from aqueous solutions.

Strontium nitrides. In the strontium-nitrogen system the following compounds are known: Sr_2N (subnitride), Sr_3N_2, Sr_3N_4 (pernitride) and SrN_6 (azide).

Strontium subnitride Sr_2N is obtained by the decomposition in a vacuum at a pressure of the order of 10^{-2} mm Hg and at a temperature of 400-500°C the nitride Sr_3N_2 in the course of 1-2 h [81]. In turn

the nitride Sr_3N_2 will be formed by heating metallic strontium in a medium of nitrogen or ammonia; nitridation begins at 380°C. This nitride can also be obtained by the decomposition of the azide SrN_6 in a vacuum.

The methods and condition of obtaining strontium pernitride Sr_3N_4 were investigated in detail in the work [82]. By the action on strontium at normal or reduced pressure of ammonia (~10 mm Hg) strontium hexammine $Sr(NH_3)_6$ with a golden color will be formed, which spontaneously decomposes at normal temperature with the liberation of ammonia and hydrogen, being converted in the compound $Sr(NH_2)_2$ with a white color; the latter at 500°C decomposes with the liberation of ammonia, yielding yellow-colored SrNH. Upon heating in a high vacuum this sequence of reactions is suppressed by the direct decomposition of the hexammine to the pernitride

$$3Sr(NH_3)_6 = Sr_3N_4 + 14NH_3 + 6H_2$$

or

$$3Sr(NH_3)_2 = Sr_3N_4 + 2NH_3 + 3H_2.$$

The second path is more preferable, since the more rapid evacuation of smaller volumes of gases occurs, but it is two-phase and less productive with respect to weight yield.

Before nitridation of raw strontium is purified by vacuum distillation at a temperature of 675-870°C, after which in a special apparatus by the action of ammonia on strontium the hexammine is obtained, which decomposes in the course of two days to the amide. The latter decomposes in a vacuum, however at a temperature of 400°C the product of decomposition contains about 65% pertnitride; a further increase in temperature leads to its decomposition with the formation of free strontium. The maximum content of pernitride, which it was possible to obtain in the products [82], does not exceed 70%, the remainder is the impurity SrNH.

The azides SrN_6 or $Sr(N_3)_2$ analogous to barium azides are obtained by preparative methods.

Strontium subnitride is a black-color powder. The measurements of its magnetic susceptibility, conducted in work [83] (Table 39), led to the conclusion about its metallic nature. The metallic bond in the lattice is provided by one of the four electrons of strontium atoms, uncompensated by their bond with trivalent nitrogen.

Table 39. The temperature dependence of the molar magnetic susceptibility of strontium nitrides.

Temperature °C	Molar magnetic susceptibility x10^6	
	Sr_3N_2	Sr_2N
20	279	155
100	250.3	145
200	250,3	11?

The increased paramagnetism of Sr_3N_2, not agreeing with the concepts, according to which this compound should be diamagnetic, is explained [83] by the presence in the preparations of iron impurities the content of which, apparently, was sharply decreased in the vacuum production from Sr_3N_2 of subnitride Sr_2N.

The measurements of the magnetic properties of the pernitride [82] showed the insignificant paramagnetism of this compound: the effective magnetic moment (in Bohr magnetons) ∿0.30 at 90°K to ∿0.60 at 673°K. The obtained data [82] attest to the salt-like, ionic character of Sr_3N_4. Two hypotheses are advanced, explaining the anomalously small value of $\mu_{эфф}$: a) the presence of antiparallel and mutually compensated spin angular momentum and orbital moment (in this case the interaction should be little affected by an increase in temperature), b) the existence of temperature-dependent equilibrium: N_4^{6-} (diamagnetic) $\rightleftarrows 2N_2^{3-}$ (paramagnetic),

severely shifted in the direction of a dimeric ion. The authors consider the second assumption less probable.

Strontium subnitride reacts with water according to equation [81]

$$Sr_2N + 4H_2O = 2Sr(OH)_2 + NH_3 + {}^1/_2H_2.$$

It is rapidly decomposed by mineral acids with the formation of the corresponding salts.

Strontium nitride Sr_3N_2 is stable compound; it melts at a temperature of 1027°C, it decomposes in a vacuum with the formation of the subnitride.

Strontium azide SrN_6 is a nonstable compound, readily giving up nitrogen with the formation of Sr_3N_2, decomposing explosively upon heating to 169°C. When shocked a weak flash occurs, accompanied by the emanation of a flame. The azide will be formed by an endothermic reaction with the absorption of heat in the amount of 49 kcal/mole.

Barium nitrides. In the barium-nitrogen system the existence of four compounds is revealed - the subnitride Ba_2N, the nitride Ba_3N_2, the pernitride BaN_2 and the azide $Ba(N_3)_2$. There are also indications of the existence the barium pernitride Ba_3N_4 [999], which is obtained by the decompoistion of barium azide $Ba(N_3)_2$.

Barium subnitride Ba_2N is obtained analogous to strontium subnitride [81], by the decomposition of Ba_3N_2 in a vacuum (10^{-3} mm Hg) at a temperature of 450-500°C in the course of 1-2 h according to the reaction $4Ba_3N_2 = 6Ba_2N + N_2 + 35.2$ cal.

Barium nitride Ba_3N_2 is prepared by heating metallic barium in air at temperatures of 260-600°C (nitridation is most conveniently at 450°C in the course of 3-4 h) [24].

Barium pernitride BaN_2 is obtained [81] by the interaction of the nitride Ba_3N_2 with nitrogen at a temperature of 400-500°C and a pressure of 200-320 at, and also by the decompostion under the same conditions of barium azide [81, 85].

The azide $Ba(N_3)_2$ will be formed by the interaction of barium hydroxide with hydrazoic acid HN_3 [1, 24, 86, 87]

$$2NaN_3 + 2H_2SO_4 = 2NaHSO_4 + 2HN_3,$$
$$2HN_3 + Ba(OH)_2 = Ba(N_3)_2 + 2H_2O.$$

Barium subnitride (a powder of black color), like strontium subnitride, is a metal-like compound with a specific electrical conductivity of the order of 10^{-2} $\Omega^{-1} \cdot cm^{-1}$ [81, 83]. It is assumed that the metallic nature is determined by a spare electron, remaining after the formation of the compound between the two barium atoms (4 electrons) and nitrogen atom (3 electrons). However, the operation of the electrons on the bond between the barium atoms in the crystal lattice is not considered at all, which also causes the relatively high electric resistance of the compound with the preservation of the negative coefficient of electrical conductivity, characteristic for metals.

Barium subnitride is decomposed by acids and water with the formation of barium hydroxide and ammonia.

Barium nitride Ba_3N_2 is black crystalline powder with a pseudohexagonal structure; it is stable under normal conditions; it is decomposed upon being heated in a vacuum; reacts with hydrogen (at 300°C), and with carbon monoxide (at 700-750°C); it is decomposed by water in cold with the formation of barium hydroxide and ammonia. The pernitride Ba_3N_4 is decomposed by water, HNO_3, and air [999].

Barium azide is unstable; it decomposes explosively at 219-225°C: upon being shocked under normal conditions it yields a weak flash with a flame; it has a monoclinic crystalline structure of the $KClO_4$ type.

2. Metal Nitrides of the Zinc Subgroup

Zinc nitrides. Nitrogen does not dissolve in solid and liquid zinc [89-91]. Zinc forms two compounds with nitrogen - the nitride Zn_3N_2 and the azide $Zn(N_3)_2$ [ZnN_6].

Zinc nitride Zn_3N_2 is obtained by heating zinc (or zinc vapors) to incandescence in a stream of ammonia for 17 h at a temperature of 500°C, then for 8 h at 550°C and 16 h at 600°C (see also [1073]). Under these conditions zinc converts to nitride without melting; about 2% of the zinc is driven off (is lost with the stream of ammonia) [24, 92]. In producing the nitride at 600°C it slowly decomposes which causes the formation of a product, depleted by nitrogen, to which can be ascribed the formula $Zn_3N_2 \cdot nZn$ [93-95]. According to Hartung [50], who heated zinc dust in ammonia for 0.5 h, the temperature zone of the formation of stoichiometric nitride is very narrow (Fig. 40), therefore it is necessary to precisely maintain the temperature regime. Thus, Bently and Sterne [97], in nitriding zinc dust with ammonia at 650°C (for 30 min) produced the nitride with a yield of 36.8%. This is explained by the admixture of free zinc in the nitride, produced under the above-cited conditions [92], which, however, is driven off at 600°C.

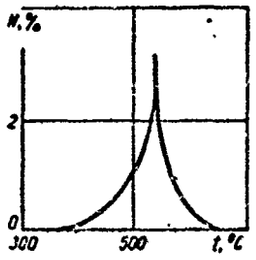


Fig. 40. The temperature dependence of the absorption of nitrogen by zinc.

Another method of preparing the nitride Zn_3N_2 is by the decompostion of zinc amide at 200°C [96]

$$3Zn(NH_2)_2 = Zn_3N_2 + 4NH_3,$$

and also by the heating of zinc cyanide with ammonium nitrate [62]

$$3Zn(CN)_2 + 12NH_4NO_3 = Zn_3N_2 + 6CO_2 + 14N_2 + 24H_2O.$$

According to [98], zinc nitride is prepared by heating a mixture of calcium nitride with zinc powder at 700-800°C.

Zinc nitride is formed by the electrolysis of water with a suspension of ammonium chloride, using a zinc anode and a platinum cathode [99]. The porous mass formed (the specific weight is 4.6 which is lower than the density of the nitride, equal to 6.22 g/cm^3) liberates upon heating nitrogen and a certain amount of hydrogen which makes it possible to assume the formation of a compound of the amide type, but not pure nitride.

Certain works [100-101] have been dedicated to producing zinc nitride by passing an electric spark between zinc electrodes in a nitrogen medium. The device, used for preparing zinc nitride in [101], is shown in Fig. 41. In glass tube A there is placed platinum cathode B, sealed in the glass. Moveable anode C is made from zinc or another metal, whose nitride it is desired to produce. The distance between the anode and the cathode is regulated by turning plug D, equipped with a screw thread. The plug is packed with mercury in can S. The lateral tubes F and G are used for collecting the nitride, forming in the lower part of the reaction tube. Into the lower part of tube A liquid nitrogen is fed and an arc is created. The zinc and nitrogen vapors are heated, the formation of the nitride occurs, which is rapidly cooled by the surplus of liquid, surrounding the arc. A mixture 1 volume of nitrogen with 9 volumes of argon is used which increases the rate of consumption of the zinc electrode.

Zinc azide $Zn(N_3)_2$ analogous to the azides of the alkaline-earth metals is produced by indirect methods [1, 9].

Fig. 41. A device for producing zinc nitride.

Zinc nitride Zn_3N_2 is powder of black-gray color;[1] it has a cubic lattice of the anti-Mn_2O_3 type, with a lattice constant of $0.74_3 \pm 0.005$ Å [102]. The molar heat capacity in the interval 298-800°K can be calculated by the equation $C_p = 19.93 + 20.80 \cdot 10^{-3} T$ (cal/mole·deg) [38]. According to [103], it is:

Temperature, °C.....	25	100	300	419.6
C_p, cal/mole·deg..... ...	26.10	27.62	31.84	34.46

The nitride is a semiconductor (Figs. 33, 42) with a resistance at room temperature of $4.5 \cdot 10^3$ Ω·cm and a width of the forbidden zone of 0.09 eV (Fig. 42, [33]).

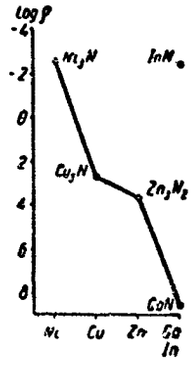


Fig. 42. The electric resistance of nitrides of certain metals [33].

Upon heating in a vacuum the nitride is decomposed to zinc and nitrogen at 300°C, at atmospheric pressure - at 700-750°C. It is

[1]The nitride, prepared by the decomposition of amides, has a greenish color.

decomposed by water with the formation of ammonia and zinc hydroxide [96], by dilute acids with the formation of ammonia and zinc salts. In air it is rather stable [92].

The azide is a highly endothermic, unstable compound, more explosive than even the azides of the alkaline-earth metals [1].

Cadmium nitrides [1026]. Nitrogen does not dissolve up to a temperature of 400°C neither in solid nor in liquid cadmium [89]. As for zinc, there are known for cadmium the nitride Cd_3N_2 and the azide $Cd(N_3)_2$.

The production of cadmium nitride Cd_3N_2 by the nitridation of metallic cadmium by ammonia is inhibited due to the high volatility of cadmium oxide and its difficult reducibility to metal. Therefore for the preparation of cadmium nitride the decomposition of the amide in a vacuum is usually used at 180°C for 36 h [106, 107, 24]

$$3Cd(NH_2)_2 = Cd_3N_2 + 4NH_3.$$

The increase in the temperature of decomposition causes the dissociation of the nitride.

Attempts were made to produce cadmium nitride by the electrolysis analogous to zinc nitride [99].

Cadmium nitride is a black crystalline substance with a cubic structure, isomorphic to anti-Mn_2O_3; the lattice parameter is a = = 10.79 ± 0.02 Å; there are 16 atoms in the unit cell [102]. It is very unstable; upon heating it decomposes at 320°C; in air it decomposes with the formation the oxide; it is explosively decomposed by water.

The azide $Cd(N_3)_2$ is still less stable than the nitride, and it explodes upon heating.

Mercury nitrides. Mercury forms with nitrogen the nitride Hg_3N_2 and the azides $Hg(N_3)_2$ and $Hg_2(N_3)_2$. The compound Hg_3N_2 is produced by passing ammonia over yellow mercury oxide heated to 100-150°C or by the indirect path from the compound NHg_2J [108, 109, 6].

The azides are also produced by indirect methods, in particular by the rapid precipitation from highly concentrated aqueous solutions $Hg(NO_3)_2$ or $Hg_2(NO_3)_2$ with the help of NaN_3. After centrifuging the residues of $Hg(N_3)_2$ or $Hg_2(N_3)_2$ are repeatedly washed with alcohol and dried in a vacuum [1074].

The nitride Hg_3N_2 is powder of brown color; it is extremely explosive; the azides have a white color and are somewhat less explosive; they dissociate readily.

An investigation of the infrared-spectra of the azides, carried out in work [1074], showed that in $Hg(N_3)_2$ the azide groups are mutually "twisted" (the symmetry is C_2), and in $Hg_2(N_3)_2$ form the highly symmetric trans-form (C_{2h}).

The properties of the metal nitrides of the zinc subgroup are given in Table 40.

Table 40. The properties of metal nitrides of the zinc subgroup.

Characteristic	Zn_3N_2	$Zn(N_3)_2$	Cd_3N_2	$Cd(N_3)_2$	Hg_3N_2	$Hg_2(N_3)_2$
Nitrogen content, wt. %	12,41	56,22	7,67	43,28	4,45	17,32
Crystal lattice	Cubic [102]	—	Cubic [102]	—	—	—
Lattice constant, Å	9,74₃ [102]	—	10,7₉ [102]	—	—	—
Specific weight: pycnometric	6,22 [102]	—	6,85 [102]	—	—	—
roentgenographic	6,60 [102]	—	7,67 [102]	—	—	—
Temperature decomposition °C	700—750	It explodes	320	It explodes	—	—
Heat formation, kcal/mole	5,3	—50,8	—38,6	—106,2	—	—100 [84]
kcal/mole	[104]	[105]	[9]	[9]		
Heat capacity, cal/mole·deg	26,10 [103]	—	—	—	—	—
Specific electric resistance, Ω·cm	4,5·10⁸ [33] (20°C)	—	—	—	—	—

CHAPTER V

NITRIDES OF TRANSITION METALS

1. Nitrides of the Rare-Earth Metals (Scandium, Yttrium and the Lanthanides)

Scandium nitrides. The most complete investigation of the conditions of the formation and certain properties of scandium nitride ScN was carried out in the work by Friederich and Sitting [110].

In attempting to obtain scandium nitride in a stream of nitrogen by the reduction of scandium oxide with carbon at a temperature higher than 1300°C a product is formed, containing only 15% nitride. Upon adding 10% ferric oxide to the initial charge the nitride content increases somewhat. A still more favorable effect is rendered by the addition of a 10% mixture of $Na_2CO_3 + 2\frac{1}{2}C$ to the initial charge that increases the nitride content in the reduction of product to 95-96% (22.6% nitrogen and 4.5 Sc_2O_3, insoluble in HCl).

The pure nitride is produced at a temperature of 1700-1800°C in a stream of well purified nitrogen according to the reaction [110]

$$Sc_2O_3 + 3C + N_2 \rightarrow 2ScN + 3CO.$$

The temperature regime was checked in [456, 467], in which chemically pure scandium oxide was mixed with carbon black and reduced in a stream of nitrogen at temperatures of 1400-2000°C.

As follows from the data of Table 41, nitridation begins at a temperature of 1400°C. However a sharp increase in the nitrogen content occurs at 1600°C; for complete reduction of Sc_2O_3 a temperature of 1900-2000°C is necessary. The products obtained here have a composition, expressed by the formula $ScN_{0.964-0.970}$; the products are contaminated with carbon and oxygen impurities. The application in the charge composition of carbonate ammonium as a loosener, facilitating the access of nitrogen, somewhat activates the nitridation process at temperatures of 1600-1700°C. But since for complete reduction of scandium oxide it is necessary to raise the temperature to 1800-2000°C, then in the final analysis the addition of carbonate ammonium is inexpedient. A product of the composition $ScN_{0.970}$ has a cubic face-centered lattice with a cell constant of $a = 4.499 \pm 0.002$ Å. It is necessary to note that the obtained nitride has a better composition than the nitride, formed by the method of [111], however, it nevertheless is a solid solution with a concentration of about 1.2% ScC in ScN.

Table 41. The composition of the reaction products of $Sc_2O_3 + 3C + N_2 = 2ScN + 3CO$ (reaction time 2 h).

Temperature, °C	Chemical composition														Conditional formula of the compound (with the addition of $(NH_4)_2CO_3$)
	Without the addition of $(NH_4)_2CO_3$							With the addition of $(NH_4)_2CO_3$							
	Sc	N	$C_{общ}$	$C_{своб}$	$C_{связ}$	Sc_2O_3	Total Sc+N+ $C_{общ}$*	Sc	N	$C_{общ}$	$C_{своб}$	$C_{связ}$	Sc_2O_3	Total Sc+N+ $C_{общ}$*	
1400	—	—	—	—	—	—	—	—	2,48	—	—	—	—	—	—
1600	—	16,71	—	—	—	—	—	76,75	20,58	1,8	1,1	0,7	0,40	99,53	—
1700	75,68	20,59	0,87	0,07	0,80	2,54	99,48	76,15	21,07	2,15	1,38	0,77	0,30	99,64	—
1800	76,99	21,18	0,70	Not detected	0,70	0,39	99,16	76,52	21,80	0,70	Not detected	0,70	Not detected	99,02	$ScN_{0.946}$
1900	76,81	22,05	0,40	The same	0,40	Not detected	99,26	76,80	22,15	0,42	The same	0,42	The same	99,37	$ScN_{0.964}$
2000	76,41	22,75	0,23	"	0,23	The same	99,39	76,52	22,62	0,25	"	0,25	"	99,39	$ScN_{0.970}$

*With the presence of Sc_2O_3 in the samples its content is included in the total.

In this work [467] the possibilities of preparing the nitride by the direct nitridation of metallic scandium were studied. The results of the nitridation of metallic scandium (Table 42), indicate that the interaction of scandium with nitrogen begins at a temperature of 500°C; at 1000°C the nitrogen content attains a value, practically not varying with a further increase in temperature. The total scandium and nitrogen content does not attain values, exceeding the scandium content in the initial metal, i.e., the oxygen, located in the metal, remains completely in the nitridation product. The ratio of the scandium and nitrogen content, neglecting the presence of oxygen, corresponds to the formula $ScN_{0.922}$, however in practice oxynitride will be formed in this case, responding to the approximate formula $ScN_{0.85}O_{0.06}$. The oxynitride has a cubic face-centered lattice with a parameter of $a = 4.503 \pm 0.005$ Å.

Table 42. The results of the nitridation of metallic scandium*.

Conditions of nitridation		Chemical composition of the nitridation products, %		
Temperature, °C	Time, h	Sc	N	Total
500	1	—	1,18	—
600	1	—	1,26	—
700	1	—	1,83	—
800	1	—	3,22	—
900	0,5	—	8,85	—
900	1	—	9,25	—
900	2	—	9,45	—
900	4	—	14,75	—
1000	1	77,98	20,11	98,09
1000	2	78,19	20,18	98,37
1000	4	78,48	20,15	98,63
1100	1	77,27	20,68	97,95
1200	0,5	77,71	20,70	98,41
1200	1	78,05	20,63	98,68
1200	2	77,30	20,75	98,05
1300	0,5	77,98	20,45	98,43
1300	1	77,43	20,85	98,28
1300	4	77,05	20,75	98,80
1400	0,5	77,85	20,42	98,27
1400	1	78,02	20,85	98,87

*The calculated composition of ScN is: Sc - 76.24%, N - 23.76%, total - 100%.

Scandium nitride is stable in air up to a temperature of 600°C, after which rapid oxidation begins, which is finally completed at 1200°C (Table 43) [466].

Table 43. The variation in the nitrogen content in scandium nitride during oxidation in air*.

Temperature, °C	Time of oxidation, h	Nitrogen content, %	Transition to Sc_2O_3, %
300	1	22,15	0
300	2	21,98	0
400	1	21,95	0
400	2	22,02	0
500	1	22,10	0
500	2	22,13	0
600	1	22,05	0
600	2	21,86	0
700	1	13,14	40,02
700	2	9,02	58,9
700	4	5,87	73,3
700	6	2,05	90,7
800	1	1,16	94,7
800	2	0,65	97,0
900	1	0,99	98,1
900	2	0,42	95,5
1000	1	0,57	97,4
1000	2	0,49	97,7
1100	1	0,13	99,4
1100	2	Not detected	100
1200	1	The same,	100
1200	2	" "	100

*The content in the original powder was N - 22.12%.

The chemical properties were studied for scandium nitride powders with the composition $ScN_{0.970}$ [466, 612] and for compact samples, prepared by the hot pressing of the nitride in graphite molds in an argon medium with respect to the conditions, given in Table 44. As can be seen from these data, the nitrogen content in the sintering process practically did not vary; the residual porosity of the samples

was from 14 to 30%. The data on the stability of scandium nitride powder in concentrated and dilute mineral acids (Table 45) show that the nitride is completely decomposed by all acids, with the exception of sulfuric, which also decomposes rather rapidly. The nitride is stable in cold and hot water; it is decomposed by an NaOH solution, where the rate and completeness of the decomposition increase with the increase in the concentration of the alkaline solution (Table 46). Compact samples of the nitride (Table 47) behave in boiling mineral acids like powder, only in sulfuric acid they decompose very slowly. The stability of compact samples in boiling NaOH solutions, where the tendency toward a reduction in stability with an increase in alkaline concentration noticeably smoothes out (Table 48).

Table 44. Conditions for sintering of scandium nitride by hot pressing*

Sintering temperature, °C	Sintering time, min	Nitrogen content in the sintered specimen, %**	Residual porosity, %
2000	4	21,78	30,1
2200	2	21,96	24,0
2200	4	21,84	23,1
2400	4	22,02	14,4

*The hot pressing of the nitride powder was carried out under a pressure of 150 kg/cm^2.

**The original powder contained 21.98% N.

Table 45. The behavior of scandium nitride powder in boiling acids.

Time, h	Undecomposed part, %	
	H_2SO_4 (1.84)	H_2SO_4 (1:1)
1	16,89	0,52
2	3,84	0,36
3	2,82	0,42

Note: Scandium nitride in boiling HNO_3 (1:1), HNO_3 (1.19), HCl (1:1) does not decompose.

Table 46. The behavior of scandium nitride powder in boiling alkaline solutions.

Time, h	Undecomposed part, %	
	10%-NaOH	20%-NaOH
1	71,94	26,01
2	71,37	18,49
4	68,93	9,59
24	—	—

Note: Scandium nitride in 40%-NaOH does not decompose.

Table 47. The behavior of compact samples of scandium in boiling acids.

Time, h	Undecomposed part, %	
	H_2SO_4 (1.84)	H_2SO_4 (1:1)
1	99,40	97,50
2	99,23	96,47
4	99,14	96,24

Note: Scandium nitride in boiling HNO_3 (1.4), HNO_3 (1:1), HCl (1.19), HCl (1:1) does not decompose.

Table 48. The behavior of compact samples of scandium nitride in boiling of alkaline solutions.

Time, h	Undecomposed part of the sample		
	10%-NaOH	20%-NaOH	40%-NaOH
1	92,03	86,25	80,04
2	90,23	81,50	78,05
4	86,11	78,43	74,90

At room temperature only nitric acid noticeably affects compact samples of scandium nitride (Table 49).

Table 49. The behavior of compact samples of scandium nitride in acids and alkaline solutions at room temperature (24 h).

Reagent	Undecomposed part of the sample, %	Reagent	Undecomposed part of the sample, %
H_2SO_4 (1,84)	100	10%-NaOH	99,34
H_2SO_4 (1:1)	100	20%-NaOH	99,00
HNO_3 (1,4)	21,8	40%-NaOH	98,65
HNO_3 (1:1)	6,7	—	—
HCl (1,19)	100	—	—
HCl (1:1)	89,9	—	—

In determining physical properties [466] samples of the composition $ScN_{0.970}$, prepared by hot pressing were used.

The microhardness of scandium nitride, measured with a load of 50 g, is equal to 1170 ± 150 kg/mm^2; the melting point, determined by the method, described in [468], is equal to 2550 ± 50°C. The coefficient of thermal expansion of the nitride, determined on a quartz dilatometer, in the temperature interval 20-1070°C is $8.68 \cdot 10^{-6}$ deg^{-1}.

The specific electrical resistance was measured for several samples of the same composition, but with different porosity; the obtained results were extrapolated the nonporous state with the use of an approximational formula, which for investigated samples had the form:

$$\rho_к = \rho_п (1 - n)^{2.8},$$

where $\rho_к$ and $\rho_п$ are the resistivities respectively of the nonporous and porous samples; n is the porosity in fractions of a unit. At room temperature the specific electrical resistance of scandium nitride is 25.4-0.9 μΩ·cm. The dependence of specific electrical resistance on temperature, determined by the method of [469], is given in Fig. 43. In the temperature interval from 20 to 1000°C the electrical resistance increases linearly with the temperature and can be described by the expression

$$\rho_t = 23 \pm 0{,}095t.$$

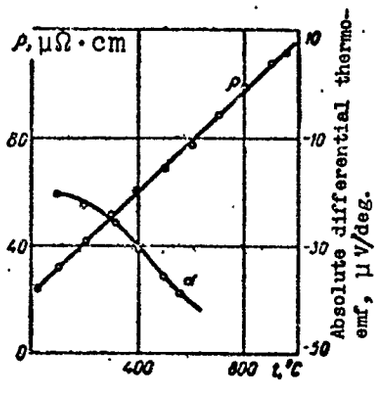


Fig. 43. The temperature dependence of electrical resistance and thermo-emf of scandium nitride.

The temperature coefficient of electrical resistance at room temperature is $+3.8 \cdot 10^{-3}$ deg^{-1}.

Comparing the values of the physical properties of scandium nitride of the composition $ScN_{0.970}$ determined in this work with source material, it is necessary to note that the melting point determined in work [466] satisfactorily coincides with that established earlier (2550 and 2650°C respectively). Scandium nitride is less refractory than the metal nitrides of group IV of the periodic system, but more refractory than the nitrides of the transition metals of groups V, VI. The value of the specific electrical resistance established in [466] is order less than that reported in [112], where the figure 308 μΩ·cm is cited. The linear increase in the electrical resistance of scandium nitride with temperature indicates the metallic nature of this compound.

The thermal coefficient of electrical resistance of scandium nitride occupies an intermediate position between the values of those for the nitrides of titanium (+2.48) and zirconium (+4.3) and is substantially higher than those for tantalum and vanadium nitrides (+0.7 and +0.03).

The thermoelectromotive force of scandium nitride has a negative value and decreases with a temperature increase which, according to [469], primarily indicates the electronic character of the on conductivity of this compound. Notice is taken of the high (for metallic conductors) absolute value of the thermo-emf of scandium nitride (from -20 to -40 μg/deg) in the temperature region of 100-600°C with low specific electrical resistance. This points to the prospect of using scandium nitride as a material for the negative arm of a thermoelectric converter turning thermal energy in electrical energy. In comparing the electrical properties of metallic scandium nitride with those for semiconductor of chromium nitride [326], it is necessary to note that for evaluating the efficiency factor of the thermoelement the important value α^2/ρ (where α is the thermo-emf, ρ is the specific electrical resistance) is greater for scandium nitride than for chromium nitride CrN (they are respectively 1.45 and 1.27 in relative units at room temperature). The value of

the thermo-emf of scandium nitride is the greatest of all values of thermo-emf for the metallic conducting nitrides of the transition metals.

Thermal conductivity of scandium nitride with the composition $ScN_{0.970}$, measured by the method of steady-state heat flow at room temperature [470], is 0.27 W/cm·deg. It is known that the thermal conductivity of a solid, caused by the thermal diffusion of free electrons, is linked with electrical resistance by the Wiedemann-Franz law $\lambda_\rho/T = 2.45 \cdot 10^{-8}$ W·Ω·deg^{-1}. For ScN with the use of established values of thermal and electrical conductivity there is obtained $\lambda_\rho/T = 2.34 \cdot 10^{-8}$ W·Ω·deg^{-1}, i.e., the thermal conduction of scandium nitride is entirely caused by the free electrons, and the role of lattice thermal conductivity as compared to electronic conductivity is insignificantly small.

Scandium nitride ScN is a dark-blue powder; its physical properties are given in Table 50. At normal temperatures ScN is stable; upon heat treating in air it is oxidized to Sc_2O_3 (lower oxides of scandium have not been established), where oxidation occurs with great difficulty. It readily dissolves in hydrochloric, nitric and sulfuric acids; upon heating with sodium hydroxide and fusing with KOH ammonia is liberated and decomposition of scandium occurs; it is readily hydrolyzed by water.

Experiments, conducted in studying the behavior of scandium nitride as an incandescent filament of an electric bulb, showed that it is completely vaporized in the course of 1 h [110].

Yttrium nitrides. Upon reducing yttrium oxide with carbon in a stream of nitrogen a nitride will be formed, containing at a reduction temperature of 1300°C yttrium nitride only in part, at higher temperatures yttrium carbide will be formed, therefore the preparation of pure yttrium nitride is difficult.

Table 50. The properties of the rare-earth metal nitrides.

Nitride	Stoichiometric characteristic		Crystallochemical properties			Thermal properties									Electrical and magnetic properties	
	Molecular weight	Nitrogen content, weight, %	Lattice constant, Å	Density, g/cm³		Melting point, °C	Heat of formation, kcal/mole [112]	Entropy, cal/deg·mole [112]	Coefficient of thermal expansion, deg^{-1} (100-700°K) [478]	Temperature, °C [74]					Specific electrical resistance, μΩ·cm (25°C)	Magnetic susceptibility χ·10⁶ (295° K)
				X-ray	pycrometric					1 mm Hg	10^{-1} mm Hg	10^{-2} mm Hg	10^{-3} mm Hg	10^{-7} mm Hg		
ScN	58,97	23,76	4,45 [111]	4,21 [111]	4,2 [475]	~2650 [111]	68,0	25	—	1880	1734	1607	1495	1230	25,4 [466]	—
YN	102,93	13,61	4,877 [113]	5,890 [113]	5,60 [113]	>2670* [113]	71,5	25	—	1990	1838	1704	1587	1230	93 [490]	—
LaN	152,93	9,16	5,30 [119]	6,845 [475]	—	—	72,1	25	$9 \cdot 10^{-6}$	2010	1855	1721	1602	—	100 [490]	+60 [478]
CeN	154,14	9,09	5,02 [118]	8,087 [118]	—	—	78,0	25	$30 \cdot 10^{-6}$	2196	2029	1884	1756	—	17 [488]	+315 [959]
PrN	154,93	9,04	5,16 [118]	7,467 [118]	—	—	—	—	$13 \cdot 10^{-6}$	—	—	—	—	—	110 [490]	+5616 [488]
NdN	158,28	8,85	5,15 [118]	7,691 [119]	—	—	—	—	—	—	—	—	—	—	75 [488, 490]	+6180 [488]
SmN	164,44	8,52	5,046 [119]	8,495 [119]	—	—	—	—	—	—	—	—	—	—	~120 [488]	+1125 [488]
EuN	166,01	8,44	5,014 [119]	8,767 [119]	—	—	—	—	—	—	—	—	—	—	~120 [488]	См. [488]
GdN	171,27	8,18	4,99₉ [119]	9,105 [119]	—	—	—	—	—	—	—	—	—	—	~200 [488]	+35600 [488]
TbN	172,94	8,10	4,93₂ [119]	9,567 [119]	—	—	—	—	—	—	—	—	—	—	~200 [488]	+42900 [488]
DyN	176,52	7,94	4,90₉ [119]	9,933 [119]	—	—	—	—	—	—	—	—	—	—	100 [490]	+48900 [488]
HoN	178,95	7,83	4,87₄ [119]	10,26 [119]	—	—	—	—	—	—	—	—	—	—	110 [490]	+47800 [488]
ErN	181,28	7,73	4,83₉ [119]	10,26 [119]	—	—	—	—	—	—	—	—	—	—	79 [490]	+36300 [488]
TuN	182,95	7,66	4,80₉ [119]	10,84 [119]	—	—	—	—	—	—	—	—	—	—	180 [488]	+23600 [488]
YbN	187,05	7,49	4,78₆ [119]	11,33 [119]	—	—	—	—	—	—	—	—	—	—	$9 \cdot 10^3$ [488]	+7250 [488]
LuN	189,00	7,41	4,76₆ [119]	11,59 [119]	—	—	—	—	—	—	—	—	—	—	360** [488]	—

*Under nitrogen.

**Weak paramagnetism, not depending on temperature.

Pure yttrium nitride was produced in [113] by the action of nitrogen on yttrium hydride YH_2 at 900°C.

In work [485] it was proposed producing yttrium nitride by the hydrogenation of the compact metal at low temperature (350-400°C), which loosens the surface, with the subsequent treatment by nitrogen at a low excess pressure 2-3 kg/cm^2 at a temperature of 1400-1600°C (see also [1075]).

Yttrium nitride is decomposed by water with the formation of hydroxide and the liberation of ammonia.

According to [1001], yttrium mononitride is not a superconductor at least higher above 1.4°K.

Lanthanum nitrides. The first experiments in producing lanthanum connections with nitrogen were undertaken by Friederich and Sittig [110]. Lanthanum nitride LaN was obtained by them by heating lanthanum oxide with carbon in a stream of nitrogen. The formation of lanthanum nitride begins at a temperature of 1300°C, and at 1500-1700°C lanthanum carbide will form [114], therefore the products prepared by this method are a mixture of nitride with carbide.

Pure lanthanum nitride is produced by heating of filings or shavings of metallic lanthanum in a stream of nitrogen [115]. Lanthanum filings, prepared in a medium of dry helium or nitrogen, are placed in a molybdenum boat, set in a furnace. At first the filings are degasified, by pumping the reaction space to a pressure of 10^{-5} mm Hg at room temperature, then nitrogen is introduced and the heating of furnace is activated. The temperature in the course of 1 h is brought up 600°C, at which temperature the reaction begins. Subsequently the temperature is increased to 750°C and held there from 2 to 4 h, then the temperature is raised to 900°C, and held there from 1 to 2 h. The full homogenization of the product is attained by holding it for 20 h at 900°C.

Lanthanum nitride was obtained by analogous method in early works [116, 117], however nitridation was carried out at somewhat higher temperatures (100°C higher according to [115]).

In the survey [24] it is reported that the nitridation of filings of metallic lanthanum at a temperature of red heat in a stream of nitrogen occurs slowly: the nitrogen content in nitridation product after 15 min is 4.4%, after 30 min – 6.0%. Complete nitridation with the production of LaN (9.18% N) is completed after 2.5 h.

The nitrides of lanthanum and the lanthanides are obtained by nitriding the metals with ammonia, where for standardization in subsequent X-ray patterns KCl (REM + 3KCl) [Translator's note: REM is rare-earth metal], was added to the metals [119]. The mixtures were placed in a quartz tube in the furnace in a corundum boat and heated in a stream of ammonia (obtained by evaporating liquid ammonia) for 3-4 h at 700°C. The nitride formed here practically corresponded exactly to the formula and had a lattice parameter of a = 5.301 Å which was rather close to the value a = 5.295 Å, [115].

In work [473] experiments were repeated for producing of lanthanum nitride by direct nitridation of metallic lanthanum. The source material was shavings of 98.5% La, prepared in an argon medium. The nitridation was carried out with ammonia and nitrogen in the reactor, described in [178].

The results of the interaction of the metallic lanthanum with the nitrogen (Fig. 44) indicate that up to a temperature of 700°C the nitridation of lanthanum with nitrogen proceeds slowly, at 700°C the nitrogen content increases immediately to a value, close to stoichiometric; with a subsequent increase in temperature and exposures of the nitrogen content practically does not vary. It is noted that the temperature of the complete saturation of lanthanum with nitrogen with the formation of LaN within the limits of the accuracy of its determination corresponds to the melting point of metallic lanthanum (826°C), where the formation of the nitride is accompanied by severe heating of the reaction mass, analogous to the production of cerium nitride (see p. 153). It was shown that for cerium and lanthanum a high ratio of heat of formation of the nitride phase to heat of fusion of the matal is characteristic (see Table 29) which, obviously, is the cause of the severe heating of the reaction mass at the melting point of the metal, and partly explains the very rapid and complete nitridation, occurring with the melting of lanthanum. Upon melting, probably, the gas-semi-impermeable nitride film is destroyed which also accelerates nitridation; at the moment of melting the atoms of the metal are in their most active state.

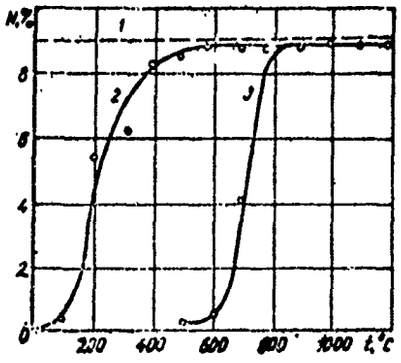


Fig. 44. The temperature dependence of the nitrogen content in lanthanum (h) (the time of nitridation is 1 h). 1 – the calculated content of lanthanum in LaN. 2 – treating lanthanum with ammonia. 3 – treating lanthanum with nitrogen.

With the use of ammonia as a nitriding agent the process of saturation of metallic lanthanum with nitrogen is essentially different from the preceding case (see Fig. 44), in the first place, by the much higher rate of nitridation at low temperatures, and also by the achievement of the maximum nitrogen content already at 600-700°C. This, obviously, is connected with the loosening of metallic lanthanum as a result of the formation and the decomposition of the hydride phases, which, according to [474], are produced even at low temperatures, and which also have cubic lattices or which are identical, or close in type to the LaN lattice. The reaction products with nitrogen, produced at temperatures of 800°C and above, and also the reaction products with ammonia, produced at 600°C and above, have a lattice of the NaCl type with a constant of: $a = 5.302 \pm 0.002$ Å.

According to Greenthal [475], for lanthanum nitride, produced by the action of liquid ammonia on lanthanum powder at low temperatures, a rhombic structure was revealed with lattice constants of: $a = 5.32$, $b = 5.30$, $c = 5.25$ Å. The pycnometric specific gravity of this nitride was equal to 4.69 which is considerably lower than the specific gravity of the nitride LaN. Obviously, the product, obtained by Greenthal, is a secondary nitride phase of lanthanum with a higher nitrogen content than in LaN.

According to Kelley [475], the standard free energy ΔF of the reaction $LaN = La + 1/2\ N_2$ in the interval of temperatures 25-800°C is $\Delta F = 72{,}100 - 25.0\ T$, cal/mole.

Lanthanum nitride is a gray to dark-gray powder. According to [126], at temperatures higher than 1.8°K LaN does not manifest superconductivity. However in the recently conducted work [479], where the superconductivity of lanthanum nitride was more thoroughly, studied, it was shown that LaN is a superconductor with a diffused region of transition between ∿1.35°K (according to magnetic measurements) and ∿4°K (according to the beginning of the anomaly of heat capacity). The existence of this region is due to the presence of two versions of lanthanum nitride which to a certain degree is confirmed by the above-cited Greenthal data.

The specific heat of LaN was determined in [480].

Lanthanum nitride is chemically unstable; it is decomposed in moist air with the liberation of ammonia; it is somewhat stabler in cold water and upon heating in water it is rapidly decomposed with the liberation of a large quantity of ammonia [131]. Upon heating in air it is oxidized to lanthanum oxide $La_2O_3 \cdot LaN$; it readily dissolves in mineral acids and alkaline solutions. Lanthanum nitride is stable for a long period of time in media of nitrogen, argon and CO_2 [473].

Crucibles, made from LaN, rapidly decompose as a result of hydrolysis [120]. Researchers [492], who studied the effect of rare-earth metals on the behavior of nitrogen in liquid iron and steels, note the role of the formation here of lanthanum nitride.

Cerium nitrides. In the cerium-nitrogen system there has been established the existence of one chemical compound with the composition CeN.

Friederich and Sittig [110] tried to produce cerium nitride by the reduction of cerium oxide by carbon in a nitrogen medium according to the reaction

$$2CeO_2 + 4C + N_2 = 2CeN + 4CO.$$

However neither at 1250°C nor at higher temperatures up to 1600°C were there detected in the reduction products of any noticeable quantities of cerium nitride.

Matignon [121] prepared cerium nitride by the reduction of CeO_2 by magnesium or aluminum in a medium of nitrogen or by the reduction of cerium chloride by sodium in nitrogen.

Vournasos [62] produced cerium nitride by the interaction of metallic cerium powder with molten potassium cyanide.

Cerium nitride can be produced by the action of nitrogen on metallic cerium [122]. The nitridation reaction at low temperatures proceeds slowly [123], but at 850°C it proceeds very energetically and is accompanied by intense heating. With the use of oxygen-free nitrogen a product with a black color with bronze iridescence will be formed.

Certain researchers have produced cerium nitride by the action of nitrogen on cerium hydride at a temperature of 800-900°C [124]. Cerium nitride is also prepared by heating of cerium carbide in nitrogen or in ammonia at 1250°C, where the reaction with nitrogen proceeds faster than with ammonia [125], which is explained by the formation of a semi-impermeable film of nitride. According to [1], cerium also absorbs nitrogen at room temperature, but very slowly.

As is reported in [129], cerium nitride is produced, like the nitrides of other lanthanides, by the nitridation of mixtures of Ce + 3KCl with ammonia during the course of 3-4 h. However in [478] this method of producing cerium nitride could not be reproduced – the nitridation products contained only 50-60% nitrogen as opposed to its content in Ce; the remaining cerium remained in the metallic state. Conversely, compact electrolytic cerium was nitrided well by ammonia at 800°C.

A detailed study of the conditions of the formation of cerium nitride was conducted in [467, 476] by the method of nitriding 98% metallic cerium in a stream of nitrogen and ammonia in a quartz reactor with double walls, between which nitrogen was passed to prevent atmospheric oxygen from getting into the reaction space. As the results of the nitridation of metallic cerium in a stream of well purified nitrogen (Fig. 45), up to 700°C showed, the cerium practically does not interact with nitrogen, and at 800°C CeN will be formed (during the course of 0.5 h), and the subsequent increase in temperature up to 1100°C does not have any effect on the composition of the nitridation product. The X-ray analysis showed that the nitridation product has a lattice of the NaCl type with a cell constant of $a = 5.023$ Å which coincides well with the tabular data.

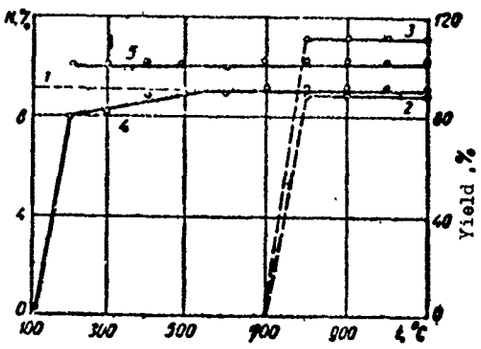


Fig. 45. The dependence of the nitrogen content in the nitridation products of metallic cerium and of the yield of nitride on temperature (the time of nitridation is 1 h). 1 — the calculated nitrogen content in CeN. 2 — the nitrogen content in the reaction products of cerium with nitrogen. 3 — The yield upon interaction with nitrogen. 4 — The nitrogen content in the reaction products of cerium with ammonia. 5 — The yield upon interaction with ammonia.

The formation of cerium nitride "spasmodically" at a temperature of 800°C agrees well with the data of work [123], in which, however, the formation temperature of the nitride is equal to 850°C. It is absolutely obvious that this temperature within the limits of the accuracy of its determination coincides with the melting point of metallic cerium (815°C). It is necessary to assume that nitridation occurs at a high rate upon the melting of cerium, apparently, due to the destruction of the very thin and nitrogen-semi-impermeable of nitride film [125] and the relatively the high vapor pressure of cerium at the melting point. As was observed in [123] and also by

us the intense heating of the reaction mass with the formation of cerium nitride can be explained by the low heat of fusion of cerium in comparison with the heat of formation of the nitride (see Table 29). This factor also determines the high rate of reaction and, probably, should be considered in all these cases of nitridation, when on the surface of the metal being nitrided a gas-semi-impermeable film will be formed. It is necessary to note the similarity of the observed effect to the phenomenon of the vigorous growth of grains upon the sintering of articles made from thoriated tungsten.

The nitridation of cerium in a stream of ammonia already begins at a temperature of 100°C. The nitrogen content sharply increases at 200°C; a nitrogen content, equal to that calculated, in CeN is attained at 700°C, subsequently not varying substantially. In this case the cerium is hydrogenated by the hydrogen of ammonia, according to [477]; the time, necessary to the hydrogenation of cerium, at 200°C is minimal, i.e., the rate of hydrogenation is greatest. Cerium hydride, apparently, prevents the formation of a continuous nitride film on metallic cerium. Furthermore, the replacement of the hydrogen in the lattice by nitrogen is beneficial in a thermodynamic regard (the heats of formation of the hydride and the nitride of cerium are equal respectively to 42.3 and 78 kcal/mole). The formation of active cerium atoms upon the dissociation of cerium hydride does not have substantial importance, since the pressure of dissociation of cerium hydrides, at least up to 700-800°C, is small.

According to [485], cerium nitride was produced by the hydrogenation of the compact metal at a temperature of 350-400°C with the subsequent treatment with nitrogen at 1400-1600°C.

In dry air and carbon dioxide at normal temperatures cerium nitride is stable; in moist air it is rather rapidly oxidized [62]. Under the effect of hydrogen on cerium nitride at 100-400°C (especially at 200°C) CeN is decomposed with the formation of cerium hydride and ammonia.

$$CeN + 3H_2 = CeH_3 + NH_3.$$

With the action of a mixture of nitrogen and hydrogen on cerium, cerium nitride will be formed, which according to the above-cited equation decomposes with the formation of ammonia. This makes it possible to examine cerium nitride as a unique catalyst of the process of binding nitrogen with hydrogen into ammonia.

The interaction of cerium nitride with water proceeds very energetically; it is accompanied by intense heating up to 700-800°C [131]

$$2CeN + 4H_2O = 2CeO_2 + 2NH_3 + H_2.$$

The CeN slowly dissolves in an aqueous solution of KON with the formation of cerium hydroxide and ammonia; upon interaction with dilute acids dissolution proceeds actively with the formation of cerium salts and ammonium

$$2CeN + 4H_2SO_4 = Ce_2(SO_4)_3 + (NH_4)_2SO_4.$$

The dissolution in certain cases is accompanied by such intense heating that part of the liberated ammonia is decomposed into nitrogen and hydrogen.

According to [126], CeN at a temperature of higher than 1.8°K does not manifest superconductivity. The standard free reaction energy of CeN = Ce + 1/2 N_2, according to Kelley [475], is equal to 78,000-25.0 T cal/mole.

The authors [959] investigated the variation in the electrical resistance of CeN at low temperatures (to 300°C). Here the normal course resistance was detected without any anomalies of the magnetic order-disorder type. It was determined that the paramagnetism of cerium nitride is caused by the Ce^{3+}; $\chi = \chi_0 + C(T-\Theta)$, where $\chi_0 = 315 \cdot 10^{-6}$, $\Theta = 85°K$, C = 2.75 Bohr magnetons.

Praseodymium nitrides. Praseodymium nitride PrN is produced by the nitridation of praseodymium at 900°C; by the action of ammonia at temperatures up to 1000°C on praseodymium carbide; by heating praseodymium in a stream of ammonia, and also by the reduction of praseodymium oxide with a magnet [Translators note: probably means magnesium] nitrogen medium [6, 9].

These investigations were continued by M. D. Lyutaya and A. B. Goncharuk, who showed that the formation of the nitride under the effect of ammonia on metallic praseodymium occurs rather rapidly. Compact samples of metallic praseodymium with dimensions of 10 × 5 × × 5 mm intensively interact with ammonia starting at a temperature of 200°C, when the nitrogen content in the nitridation product attains 6.5%, and after one-hour effect of ammonia at 400°C the praseodymium is completely converted to a nitride of stoichiometric composition, where the sample is scattered in a powder or fine pieces of the nitride. Nitridation by ammonia at a temperature of 600°C leads to the transition of the metal into the nitride with cracking of the samples, and at 700°C – to the production of compact samples of the nitride with the preservation of the shape of the original metallic sample. With a further increase in the temperature of the nitridation with ammonia the nitrogen content in the samples of praseodymium sharply decreases and composes at 800°C – 1.5%, and at 1000°C – 1.8%. The rapid nitridation at low temperatures can be connected with the loosening action of the simultaneously forming hydride. At high temperatures the rate of decomposition of the hydride is higher than the rate of its formation which causes a sharp reduction in the rate of nitridation and practical cessation of hydrogenation.

Praseodymium nitride is a black-colored substance, unstable in air under normal conditions, which hydrolyzes rapidly [131]. According to [989], the Curie point is PrN θ = - 11°K, the magnetic moment is 3.57 Bohr magnetons.

Neodymium nitrides. The neodymium nitride NdN is produced by the methods, mentioned above for praseodymium nitride, and under the same temperature conditions. In [1] the producing of neodymium monoitride is indicated by the effect of very pure ammonia on metallic neodymium at a temperature of 700°C during a period of 3-4 h. The chemical properties of neodymium nitride are analogous to the properties of praseodymium nitride.

T. S. Verkhoglyadova showed that upon nitridation of neodymium by nitrogen the nitride will be formed after 2 h at 800°C and after 15 min at 1000°C. It is interesting that it was possible to repeatedly produce, especially at temperatures of 1050-1200°C, praseodymium neodymium nitrides with a considerably greater nitrogen content than is required by the formula MeN. These products corresponded to the conditional formulas $MeN_{1.7-1.8}$ (a nitrogen content up to 14-14.5 weight %). Thus the praseodymium and neodymium atoms have in the isolated state f-electron configurations of $4f^3$ and $4f^4$ respectively, which can be readily transferred to a partner with a transition to the stable f^0-state, then the obtained experimental results seem logical.

The authors of work [1075] demonstrated that in the nitridation of compact samples of metallic neodymium with ammonia the interaction begins at 300°C, and at 500°C a compact sample of neodymium nitride will be formed. An increase in the temperature of nitridation of the metal causes a sharp reduction in the nitrogen content. The causes of the increase in the temperature of nitridation of neodymium are analogous to those in the nitridation of compact praseodymium (see above).

The researchers [485] produced neodymium nitride by the hydrogenation of the compact metal at 350-400°C with subsequent treatment with nitrogen at 800-1600°C. In work [481] the electrical resistance and the thermo-emf of neodymium nitride (a = 5.126 Å) at low temperatures were investigated. The temperature dependence of electrical resistance (Fig. 46, curve 1) is an expression of integral

resistance: $\rho = \rho_1 + \rho_2 + \rho_3$, where ρ_1 is the fraction of electrical resistance, caused by defects and impurities; ρ_2 is the fraction of electrical resistance, caused by the scattering of phonons; ρ_3 is the fraction of electrical resistance, caused by the disordering of the spins. On the same graph the calculated values ρ_2 (curve 2) and ρ_3 (curve 3) are plotted. At absolute zero ρ_1 = 84 μΩ·cm, and value ρ_0 = 12 μΩ·cm. The thermo-emf of the nitride in this whole region of temperatures is negative (Fig. 47) and at a temperature of 60°K α is a -0.17 μV/deg.

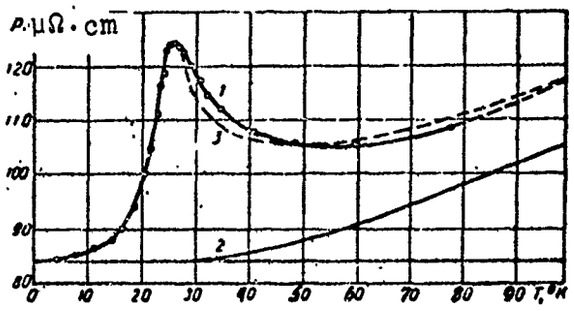


Fig. 46. The temperature dependence of the electrical resistance of neodymium; – 1 – experimental curve. 2 – the fraction of the resistance, caused by the scattering of phonons. 3 – the fraction of the resistance, caused by the disordering of the spins.

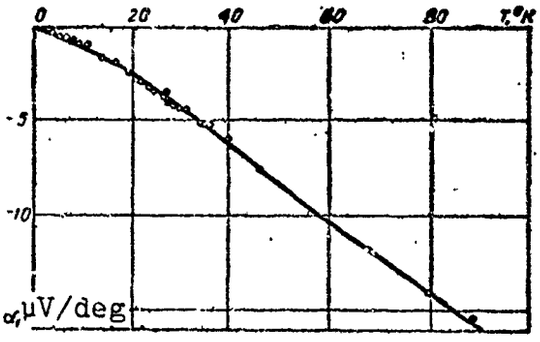


Fig. 47. The temperature dependence of the thermo-emf of NdN.

In this work the conclusion concerning the semimetallic nature of neodymium nitride was made and the presence in NdN, as in the other lanthanide nitrides [482] of a magnetic superlattice was confirmed. The Curie point of NdN is $T_c \approx 27°K$ [480].

Samarium nitrides. The methods of production of samarium nitride SmN are analogous to the methods of production of praseodymium nitride. In addition to that SmN has been prepared by the action of ammonia at a temperature of 700°C for 3-4 h on metallic samarium [119].

Researchers [128] have prepared of samarium nitride in the following manner. Samarium shavings in a molybdenum boat were placed in the tube of a vacuum furnace, in which titanium shavings (as an oxygen absorber) were simultaneously located. The tube was pumped to a pressure of 10^{-5} mm Hg and held at this pressure for 4-6 h. Nitrogen from a cylinder was passed through the heated titanium. The closed system was held for 12-16 h at 800°C. The product of nitridation was collected in a receiver filled with dry argon.

Iandelli [129] produced samarium nitride by heating metallic samarium (99.2-99.7%) at 1000°C in a molybdenum boat in a nitrogen medium. Metallic samarium was prepared by the vacuum distillation of samarium by an aluminothermic-reduction reaction of the oxide Sm_2O_3 at 1500°C. The nitridation reaction of samarium proceeds much slower than that of lanthanum, cerium, praseodymium and neodymium, and a content in the nitridation products of 94-95% SmN is attained only after 15-20 h. Nitridation is hampered by the formation on each particle of the metal of a thick gas-impermeable nitride film.

Samarium nitride is a hard powder; it is rapidly hydrolyzed in air, and it is assumed that the hydrolysis proceeds according to the reaction

$$SmN + 3H_2O = Sm(OH)_3 + NH_3.$$

However the experimentally determined weight increase of the samples does not coincide with that calculated by this equation. The

assumption that this is caused by the arrest of ammonia in the solid phase, also was not confirmed. The X-ray analysis of the products, located in air for one week, showed their amorphism. Detailed investigations of both the hydrolysis process of samarium nitride, and also of the dehydration process of the hydroxide, establish that upon hydrolysis of the nitride hydrated hydroxides $Sm(OH)_3 \cdot 2.8H_2O$ and others will be formed.

Samarium nitride has a cubic face-centered lattice with a parameter of the unit cell, according to various authors of: a = = 5.0481 ± 0.0008 [128], 5.039 ± 0.003 [129], 5.046 ± 0.001 Å [119].

Upon heating samarium nitride to a temperature of 1600°C in a vacuum of 10^{-5} mm Hg its vaporization or dissociation was not revealed [128].

Europium nitrides. Only the compound of europium with nitrogen EuN was obtained by the nitridation of metallic europium with ammonia during a period of 3-4 h at 700°C [119], and also by the direct action of nitrogen on europium under the same conditions, which are described above for samarium nitride [128]. Europium nitride is a substance of black color, and in chemical behavior is similar to the other rare-earth-metal nitrides. In [119] to determine the possibility of the existence of bivalent europium in the nitride the latter was decomposed by water, however the liberation of hydrogen with the products of decomposition was not noticed neither for europium nitride nor for samarium and ytterbium nitride.

Gadolinium nitrides. Gadolinium nitride GdN is produced by nitriding metallic gadolinium with pure ammonia for 3-4 h at a temperature of 700°C [119]. Endter [130] by X-ray analysis detected GdN in the surface layer, forming upon the heating of gadolinium in air.

Gadolinium nitride is a black-colored substance with a cubic structure; its chemical and physical properties have almost not been studied. Gadolinium nitride is a ferromagnetic material with a Curie point of 69°K and ferromagnetic moment of 7 Bohr magnetons, equal to the paramagnetic moment. Under pressure of up to 100 kbar the variation in the Curie point is for GdN $\partial T_c/\partial P = +0.08° \pm 0.04°K$ [1007]. In work [1008] the spontaneous magnetization of this nitride was investigated.

Nitrides of terbium, dysprosium and holmium. The information about the nitrides of these metals is very limited. TbN, DyN and HoN have been prepared by the action of ammonia for 3-4 h at a temperature of 700°C on the respective metals [119]. An attempt to produce dysporsium nitride by the reduction of dysprosium oxide with carbon in a nitrogen medium did not give positive results; formed product was not monophase [110].

In work [483] terbium and holmium nitrides were produced from the pure metals (99.5%), which were first hydrogenated, and then the hydrides were nitrided with ammonia at temperatures of 850-1100°C. Chemical analysis showed that the preparations contained more than 95% of the nitrides.

The properties of these nitrides have almost not been studied; in [119] their crystal structures are given.

According to [153], TbN and HoN are ferromagnetic materials with Curie points respectively of 18 and 43°K; the magnetic moment of HoN is 8.0 ± 1.0 Bohr magnetons [475]. On the basis of the study of the magnetic properties of TbN in [484] a conclusion is drawn about the fact that an electron is transferred from N^{3-} to Tb^{3+}, giving the nitrogen an antiparallel spin.

Erbin nitrides. With the reduction of erbium oxide with carbon in a nitrogen medium

$$Er_2O_3 + 3C + N_2 \rightarrow ErN + CO$$

a product is obtained, containing about 50% ErN, and upon the addition to the charge of a 10% mixture of soda with carbon (see scandium nitrides, p. 136) at a temperature of 1250°C an almost pure nitride will be formed.

As is reported in [119], erbium nitride is prepared by the action of ammonia at 700°C for 3-4 h on metallic erbium.

Erbium nitride of ErN is a grayish-white-colored substance; it is gradually decomposed in air with the liberation of ammonia; its decomposition is completely finished within several days.

The physical properties of erbium nitride have not been studied (only its crystal structure has been determined [119]).

Thulium nitrides. The only mention of thulium nitride TuN [TmN] is in [119]. It is formed, analogous to the other rare-earth-metal nitrides, by the action of ammonia on metallic thulium at 700°C.

Ytterbium nitrides. The first attempts at the production of ytterbium nitride YbN were made by Friederich and Sittig [110] who, however, were not able to prepare the pure nitride by the reduction of ytterbium oxide with carbon in a nitrogen medium at temperatures of 1100-1600°C.

In work [119] ytterbium nitride, like the nitrides of the other lanthanides, were obtained by the action of ammonia on metallic ytterbium at 700°C.

Eick with his colleagues [128] prepared ytterbium nitride analogous to the samarium and europium nitrides (p. 158) by the action of nitrogen on metallic ytterbium, however the formation reaction of ytterbium nitride in contrast to the samarium and europium nitrides occurred so slowly that it was necessary to reject this method. The method of preparing ytterbium hydride with its subsequent conversion to nitride was used. Ytterbium shavings were

treated for 12 h at a temperature of 500°C with pure hydrogen, obtained by the decomposition of uranium hydride UH_3. The hydride formed YbH_2 was heated in a stream of nitrogen, purified by being passed over activated copper and titanium shavings, at temperatures of 600-1000°C for 12 h. Even with very long exposures and nitridation temperatures of the order of 1000°C (which is 200°C higher than the melting point of ytterbium) the reaction does not occur completely. In an attempt to drive off metallic ytterbium from the nitride in a vacuum of 10^{-5} mm Hg turned out that upon sufficiently prolonged exposure at 1400°C the metal and nitride are converted into a distillate. Thus, ytterbium nitride is readily vaporized in a vacuum which distinguishes it from the nitrides of certain other lanthanides, in particular samarium.

Ytterbium nitride has a cubic structure of the NaCl type with a lattice parameter of $a = 4.786 \pm 0.001$ Å according to [119] or $a = 4.8752 \pm 0.0008$ Å according to [125].

In work [119] the liberation of hydrogen was not detected with the action of ytterbium nitride of water which attests to the absence of bivalent ytterbium nitride.

Lutetium nitrides. Lutetium nitride of LuN is produced by the action of ammonia on metallic lutetium at a temperature of 700°C [119].

The structures and physical properties of rare-earth-metal nitrides. All nitrides of the rare-earth-metals, including scandium and yttrium, crystallize in a cubic face-centered lattice of the NaCl type and correspond to the composition MeN. Compounds of other composition in the rare-earth-metal system with nitrogen have not been detected. The formation of rare-earth-metal mononitrides with a simple lattice agrees well with the values of the ratios of the radius of the nitrogen atom to the radii of the rare-earth-metal atoms, being in accordance with the data of Table 51 from 0.34 to

0.43 which corresponds to the Hägg condition of the formation of simple structures of the interstitial phase type.

Table 51. The ratios of the radius of the nitrogen atom to the radii of the rare-earth-metal atoms.

Metal	$R_N:R_{Me}$	Metal	$R_N:R_{Me}$	Metal	$R_N:R_{Me}$
Sc	0,43	Pm	0,39	Ho	0,40
Y	0,39	Sm	0,38	Er	0,40
La	0,37	Eu	0,34	Tu	0,40
Ce	0,38	Gd	0,39	Yb	0,36
Pr	0,38	Tb	0,40	Lu	0,40
Nd	0,38	Dy	0,40		

The dependence of the lattice constants of nitrides on the atomic number of the rare-earth elements (Fig. 48) [119] displays the effect of lanthanide contraction. The sequence of this dependence is analogous to the sequence on effect in the lattice constants of rare-earth-metal oxides, which attests to the significant role of ionic bonding in nitrides. This also indicates the absence of anomalies in the lattice constants for europium and ytterbium, which in the metals themselves and metallic type compounds (hexaborides and dicarbides [486]) have increased significance in connection with a valance of Eu and Yb less than +3, manifested in the metallic state. A certain anomaly for gadolinium nitride, coinciding with a similar anomaly for gadolinium oxide (also emphasizing the similarity in the types of chemical bonding in the lattices of these bonds), is caused by the effect of the semioccupied electronic configuration Gd^{+3} (7 electrons of 14 on the 4f-level). The latter along with the configurations of lanthanum ($4f^0$) and lutetium ($4f^{14}$) is the stablest and ensures the exact trivalence of the gadolinium ion in contrast to the other lanthanides, where mixed valence gives them certain attributes of metallicity.

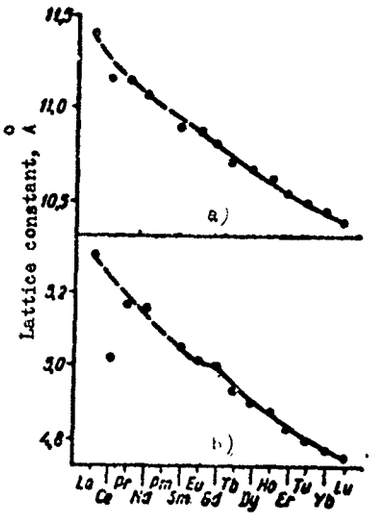


Fig. 48. Lattice constants. a) of oxides. b) of lanthanide nitrides.

According to the magnetic measurements, carried out by Essen and Klemm [478], the lanthanum in lanthanum nitride is also completely in the form of La^{+3} ions, when the approximate content of Me^{3+} ions in cerium nitride is approximately 11%, and in praseodymium nitride – about 62%. The remaining atoms of the metallic components are in the form of Me^{4+} ions.

Connected with the high content of Me^{4+} ions in cerium nitride are certains deviations from the normal sequence of a curve of lanthanide contraction, observed in certain works, in particular, the dimension of the unit cell of CeN in Iandelli's work [129] is examined from this point of view.

The deficiency of data about the physical properties of rare-earth-metal substantially hampers the discussion of the nature of their electronic structure. However even from the preceding considerations it follows that they are compounds of the ionic type which is caused by the high ionization potentials of nitrogen, bringing about the intense negative polarization of the cores of nitrogen atoms, as was shown, in particular, by the works of Klemm [119] based on the calculation of the additional participation in the interatomic distances of the lattice of the radius of the N^{-3} ion. For scandium and yttrium nitrides the degree of polarization should be considerably less than in the lattices of the lanthanum

and the lanthanide nitrides, and it is possible to expect for these two nitrides a smaller fraction of ionic bonding. From ScN to CeN the asymmetry of the distribution of electron density increases, if one were to judge from the increase in the vapor pressure and the heats of formation in accordance with the concepts, expounded in [4] that attests to an increase in the fraction of the ionic bonding component. Undoubtedly, the nature of conductivity should simultaneously vary, connected with the variation in the width of the energy gaps, peculiar, especially for the nitrides of the second half-period of the lanthanides, to semiconductors, in this case of the $A^{III}B^{V}$ type.

These considerations are also confirmed by other data on the physical properties of lanthanide nitrides. Thus, Daou [487] showed that the ratio of electrical resistance $R_{MeN}:R_{Me}$ increases in the transition from cerium to praseodymium from 1.66 to 30 (at 25°C) which, obviously, is connected with the greater relative delocalization of the valence electrons of praseodymium in the formation by it of a bond with nitrogen and in the tendency to be converted to a stable f^0-state. Up to 500°C for cerium nitride there was detected a sequence of resistance, typical for metals with an increase in the ratio $(R_{MeN}:R_{Me})_{500°C}/R_{MeN}:R_{Me})_{250°C}$ by approximately four times. For praseodymium this increase is practically absent (Fig. 49).

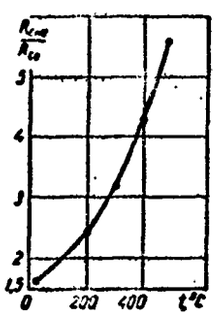


Fig. 49. The temperature dependence of the ratio $R_{CeN}:R_{Ce}$.

It is necessary to note the increase in magnetic susceptibility from lanthanum nitride to neodymium nitride, established in [478]. It is characteristic that an especially sharp increase of χ is

observed in the transition from cerium nitride to praseodymium nitride which corresponds to a sharp variation in electrical resistance (Fig. 50).

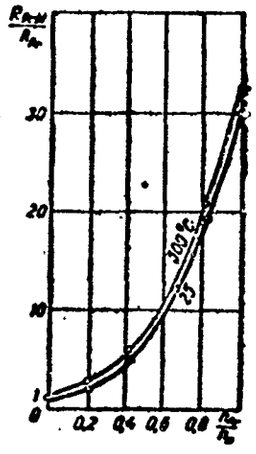


Fig. 50. The dependence of the ratio $R_{PrN}:R_{Pr}$ on the nitrogen content (n are the atomic fractions).

A detailed investigation of the magnetic properties of the rare-earth-metal nitrides was conducted [488]. The magnetic moments of the mononitrides were close to the magnetic moments of the three positive ions of the rare-earth-metals which, as also in the case of the sulfides Me_2S_3 [489], indicates a considerable component of ionic bonding in these compounds. The dependence of the magnetic moments of nitrides on the atomic number of the rare-earth-metals is analogous to that for sulfide. It is characteristic that an especially sharp increase in magnetic susceptibility is observed in the transitions from CeN to PrN, from SmN to EuN and from TuN to YbN which corresponds to the sharp variation in electrical resistance.

A more detailed investigation of the electrical properties of the rare-earth-metal nitrides, was carried out in [491]; the presence of energy gaps (with respect to the absorption edges, located on the curves of optical transmission) was actually detected the lanthanide nitrides: DyN – 2.60-2.90 eV, ErN – 2.40-2.78 eV, HoN – 1.70-1.88 eV. Electrical resistance within the limits of from 80 to 1500°K has a metallic character which is explained by the great

concentration of current carrier-electrons, which is caused by deviations from stoichiometry with respect to nitrogen content [491]. Thus, these nitrides are degenerate defect (due to an excess of electropositive lanthanide atoms) semiconductors with a broad energy gap. For ScN and YN investigated in the same work no definite absorption discontinuity was detected which obviously, is caused by the high donor ability of these metals and by the formation of a typically metallic bond, accomplished by the collectivized electrons of the metal and the nitrogen. Similar conclusion were also confirmed by X-ray spectral investigations of ScN [960].

The data on the electrical properties of the lanthanide nitrides agree with the data, obtained by Didchenko and Gorstema [488], although the latter conducted measurements on nitrides of stoichiometric composition. This varience should be removed by further investigations, however it seems to us that the concepts, developed in work [491], are more preferable. However, naturally, it is impossible to expand these concepts scandium and yttrium nitrides which are typical metallic phases.

Ytterbium nitride, according to [488], differs from the other lanthanide nitrides by a negative temperature coefficient of electrical resistance, characteristic for semiconductors.

In Fig. 51 the dependence of the electrical resistance of rare-earth-metal nitrides on the atomic number at room temperature is shown [488].

In Fig. 52 the temperature dependence of the electrical resistance of pressed powders of certain nitrides is given. The data for Ce do not yield to rational interpretation as regards to lanthanum and praseodymium nitrides, then they display in the region of low temperatures typical metallic conductivity. The authors [478] perceive in the behavior of CeN a reflection of the high content in it of Ce^{4+} ions. The semimetallic character of cerium mononitride is discussed in [490].

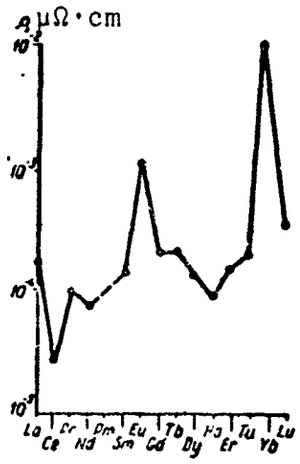


Fig. 51. The dependence of the electrical resistance of nitrides on the atomic number of the lanthanides.

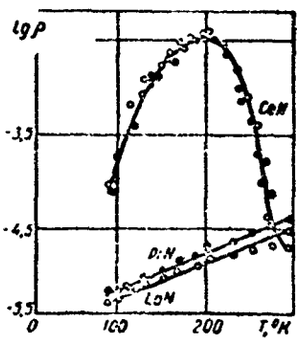


Fig. 52. The temperature dependence of the electrical resistance of pressed powders of lanthanide nitrides.

It is characteristic that in the transition from LaN to CeN the coefficient of thermal expansion increases very sharply – from 9 to $30 \cdot 10^{-6}$, and subsequently for praseodymium nitride it again rather intensely decreases – to $13 \cdot 10^{-6}$ [478] which corresponds to the weakening of the Ce – Ce bonds and to the strengthening of the Ce – N bonds, which was indicated above.

2. Transition-Metal Nitrides of Group IV

Titanium nitrides. From the phase diagram of the titanium – nitrogen system, plotted according to [132] (Fig. 53), it follows that titanium forms with nitrogen a nitride, corresponding to the formula TiN, possessing a broad region of homogeneity, and also a nitride, corresponding to the ε-phase.

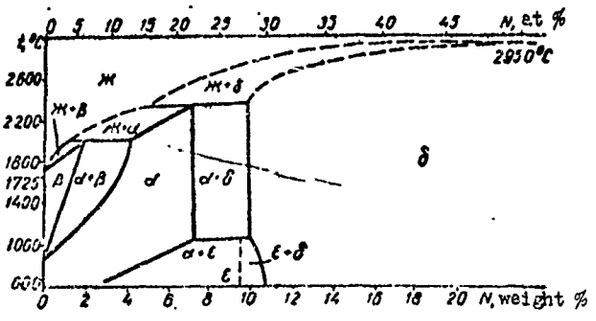


Fig. 53. Phase diagram of the titanium – nitrogen system.

Four phases are detected in the system: β, α, ε and δ. The peritectoid β-phase contains (at 2020 ± 25°C) about 1.4% N and forms upon reaction between the α-phase and the melt: $\alpha+Ж \rightleftharpoons \beta$. At the same temperature the α-phase is homogeneous within the limits of 6.5-7.4% N; it forms according to the peritectic reaction $\delta+Ж \rightleftharpoons \alpha$ at 2350 ± 25°C. The ε-phase, to which is ascribed the arbitrary formula Ti_3N, forms according to the peritectic reaction $\alpha+\delta \rightleftharpoons \varepsilon$ at temperatures of 1000-1100°C; it is homogeneous within the limits of 6.8-8.9% N; it has an tetragonal lattice with unit cell parameters of: a = 4.92 kX; c = 55.61 kX, c/a = 1.05 [132].

The solubility of nitrogen in α-Ti at the temperature of the peritecoid reaction lies within the limits of 6.5-7.4%. The addition of nitrogen to the titanium causes an increase in the temperature of the $\alpha \rightleftharpoons \beta$ transformation, i.e., the nitrogen stabilizes the α-titanium. A theoretical investigation of the temperature dependence of the solubility of nitrogen in titanium on the ratio of the atomic radii of titanium and nitrogen, and also of the electron structure of the solid solutions forming was carried out in [133, 134]. The activation energy of the diffusion of nitrogen in the α-phase is 68,000 kcal/mole [1119].

Holberg [235] established that the maximum solubility of nitrogen in α-titanium is about 17 at. % ($TiN_{0.20}$). He detected the nitride phase Ti_2N (ε-phase), to which was earlier assigned the

formula Ti_3N. This phase has a tetragonal lattice of the antirutile type (space group $P4_2/mnm$) with two formula units in the unit cell with lattice parameters of a = 4.9452, c = 3.0342 Å.

The dissolution of nitrogen in titanium linearly changes the lattice parameters of α-titanium: greater than with the dissolution of oxygen, and somewhat less than with the dissolution of carbon [205]. Consequently, the measurement of the parameter of a crystal lattice can serve as a reliable method for determining small contents of nitrogen in titanium.

The region of homogeneity of titanium nitride TiN, according to [132], is 10-22.6% N. According to Ehrlich [135], the lower limit of the region of homogeneity corresponds to an alloy with 10.9 weight % of N or the formula $TiN_{0.42}$, and according to [235] which, apparently, is more reliable – to the formula $TiN_{0.60}$ (14.8 weight % of N). The upper boundary of the region of homogeneity of this compound can be accepted as 50 at. % of N, i.e., it corresponds to the formula $TiN_{1.0}$ [132]. However it is necessary to note that in the early works (Breger [136], and then Münster and Sagel [137]) a higher upper limit of the region of existence of this nitride is indicated, corresponding, according to [136], to the formula $TiN_{1.16}$, which is relatively close to the composition of the valence compound Ti_3N_4, which would be formed with an ionic character of binding between Ti^{4+} and N^{3-}. Consequently, the formation of titanium nitride with a nitrogen content of more than 50 at. % is on indication of the tendency of titanium to ionic bonds with nitrogen which is caused by the high ionization potential of nitrogen. The purely crystallochemically nitride phases of titanium with an excess of nitrogen (or deficiency of titanium) it is necessary to examine, according to Ormont, as solid solutions of nitrogen in nitride, structured according to the principle of subtraction. The correctness of the concepts about nitrides with an excess of nitrogen, as those about solid solutions of subtraction, Breger confirmed by analyzing the intensities of the interference lines on X-ray photographs by the method, accepted in the works of Umanskiy and Khidekel concerning

titanium carbide and Umanskiy concerning vanadium carbide [138]. The formation of such phases Breger associates with the method of their production, consisting in the dissociation of amminochlorides of the $TiCl_4 \cdot 4NH_3$, type, which at low temperatures does not proceed to the end, so that part of the excess nitrogen atoms remains in the lattice and is removed only after heating to high temperatures of the order of 1500°C. To this assertion one should add that the formation of phases with surplus of nitrogen, having features of ionic bonding, is assisted by the ionic state of titanium in the amminochloride.

The X-ray spectral investigation of titanium nitride of saturated composition and in the region of homogeneity [227-229] showed that with an increase in the nitrogen content in the region of homogeneity of titanium nitride a change in the character of the chemical bond occurs in the direction of increasing its metallic component. Interatomic interaction in the nitride is accomplished with very little participation of the d-orbits of titanium with mobilization of mainly the external s- and p-orbits of both atoms. This conclusion agrees with the contemporary concepts about the nature of the electron structure of titanium nitride (see p. 15), if by metallic bonding there is implied a bond, accomplished by an exchange between the nonlocalized electrons and the electrons, entering into the composition of stable configurations, formed by electrons, localized near the titanium and nitrogen atoms. In connection with the relatively low statistical weight of the d^5-configurations of titanium atoms (43%) the fraction of electrons, located in the nonlocalized state (mainly 4s-electrons), for it is great. Furthermore, nitrogen atoms having an s^2p^3-configuration in the isolated state, tend to acquire a quasi-stable sp^3-configuration with the transfer of one p-electron to the nonlocalized state. Thus, the electrons of the d-shell of titanium practically do not participate in a metallic bond. From this point of view an increase in the metallic component of a bond with an increase in the nitrogen content in the region of homogeneity of titanium nitride can be interpreted, as an increase in the statistical weight of the nonlocalized electrons in stable configurations with the simultaneous removal of electrons from the covalent bonds between the titanium atoms.

It is obvious that the ionic fraction of the bond in titanium nitride is determined by a certain probability of the attraction by the nitrogen atoms of titanium electrons with the formation of s^2p^6-electron configurations. The statistical weight of the latter in preparations of titanium nitride, obtained from amminochloride is especially great, where these configurations are formed by the chlorine atoms and by the nitrogen atoms and are preserved in the nitride.

With an increase in nitrogen in the region of homogeneity of titanium nitride both the parameter of the crystal lattice and the density are changed (Fig. 54, Table 52), as well as all the physical and chemical properties which is very essential for its practical application.

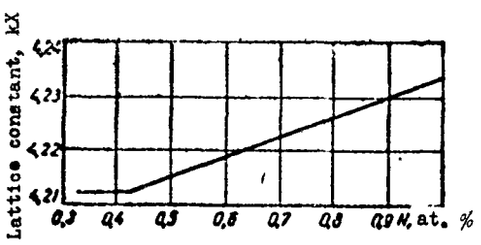


Fig. 54. The dependence of the lattice constant of titanium nitride on the nitrogen content in it.

Table 52. Variation in the density and molar volume of titanium nitride in the region of homogeneity [135].

Composition	Density, g/cm^2	Molar volume, $cm^3/mole$
$TiN_{1.00}$	$5,21_3$	11,87
$TiN_{0.70}$	$5,10_2$	11,31
$TiN_{0.44}$	$4,87_6$	11,10

The properties of titanium nitride of saturated composition, corresponding to the formula TiN, were described in detail in the reference books [139, 140], and in the region of homogeneity – they are given in Table 53. Therefore in the present section we will dwell only on certain properties, having a fundamental character.

Table 53. The physical properties of titanium nitride within the limits of the region of its homogeneity [145, 147].

Arbitrary formula	Content of N		Thermo-emf α, μV/deg	Hall coefficient $R \cdot 10^4$, cm^2/C	Specific electrical resistance ρ, μΩ·cm	Microhardness H_M, kg/mm^2
	weight %	at. %				
$TiN_{0.557}$	14,0	35,8	—	—	112,5	—
$TiN_{0.59}$	14,7	37,1	+0,9	+2,5	—	1200±137
$TiN_{0.6}$	14,9	37,5	+0,5	—	91,2	—
$TiN_{0.63}$	15,7	39,1	—	—	—	1440±182
$TiN_{0.65}$	15,9	39,5	—0,75	+1,9	70,6	—
$TiN_{0.69}$	16,7	40,8	—1,88	+1,5	60,5	—
$TiN_{0.745}$	17,8	42,7	—3,6	+0,9	50,6	—
$TiN_{0.78}$	18,7	44,3	—4,3	—	—	—
$TiN_{0.84}$	19,7	45,8	—5,34	—	—	—
$TiN_{0.85}$	19,9	46,1	—	—	—	1630±101
$TiN_{0.88}$	20,4	46,8	—	—0,37	—	—
$TiN_{0.91}$	21,0	47,6	—	—	31	—
$TiN_{0.92}$	21,4	47,9	—	—	—	1780±51
$TiN_{0.95}$	21,7	48,7	—7,1	—0,63		—
$TiN_{0.97}$	22,2	49,3	—	—		1900±182
$TiN_{0.98}$	22,4	49,8	—7,38	—0,67	2[illegible]	1994±137

Physical properties. Titanium nitride in the powdery state is a yellow-brown color; after sintering in the compact state it acquires a characteristic golden-brassy color. In the compact state it buffs and polishes well.

The thermal properties of titanium nitride within the limits of temperatures of 298-1800°K were investigated by Naylor [141], according to whose data

$$H_T - H_{298,16} = 11{,}91T + 0{,}0004T^2 + \frac{296000}{T} - 4585 \text{ [kcal/mole]},$$

$$C_p = 11{,}91 + 0{,}00094T - \frac{296000}{T^2} \text{ [cal/deg·mole]}.$$

According to Sato [142], the specific heat, measured on impure preparations and corrected for pure nitride within the limits of 0-500°C, is:

$$C_p = 0{,}1410 + 1{,}918 \cdot 10^{-4} T - 1{,}127 \cdot 10^{-7} T^2.$$

The specific heat at low temperatures, according to [143], is as follows:

T, °K	52,5	60,5	69,7	78,5	94,9	125,2	145,8	165,7
C_p, cal/mole	0,527	0,809	1,189	1,582	2,331	3,704	4,577	5,358
T, °K	185,7	206,0	226,3	246,0	266,1	286,2	298,16	
C_p, cal/mole	6,073	6,705	7,286	7,768	8,234	8,642	8,86[1]	

Researchers [110], in determining the vapor pressure of titanium nitride, noted its difficult vaporizability even at temperatures, close to the melting point. The results of the quantitative investigations, carried out by Kelley [150], and given in Deshman's summary [74] in Table 14, show that near the melting point the dissociation pressure of the nitride does not exceed 1 mm Hg. Data on the vapor pressure of titanium nitride are also given in [45].

Pollard and Woodwart [158] determined the dissociation pressure of titanium nitride on preparations, obtained by accumulation from the gaseous phase on a tungsten wire. Corresponding the data for the temperatures 1200 and 1450°C are given in Fig. 55. According to these data the thermal dissociation of titanium nitride is a second order reaction, the rate constant of which obeys the equation

$$K = \frac{1}{\tau} \cdot \frac{x}{a(a-x)} \quad [\text{mm Hg}^{-1} \cdot \text{min}^{-1}],$$

where a is the gas concentration at maximum pressure p_0, x is the gas concentration at pressure p, τ is the time. Given below are the values of the rate constant of dissociation of titanium nitride by time at a temperature of 1200°C (p_0 = 0.59 mm Hg):

τ, min	5	10	20	30	40	50	60	70	80	90
K, $мм\ Hg^{-1} \cdot min^{-1}$	0,19	0,23	0,23	0,22	0,22	0,23	0,22	0,22	0,23	0,23

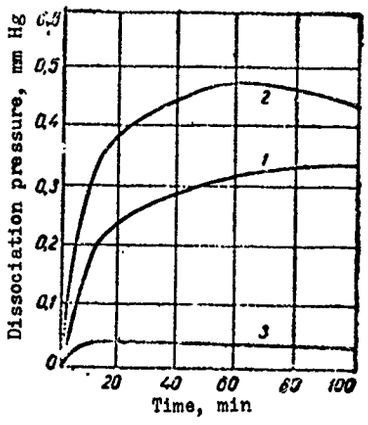


Fig. 55. Dissociation pressure of TiN. 1 – TiN on a tungsten wire at 1200°C. 2 – the same at 1450°C. 3 – tungsten wire at 1200°C (standard without titanium nitride).

Subsequent investigations of the behavior of titanium nitride in a vacuum were carried out in work [203], in which the vaporization of TiN was determined by the Knudsen effusion method at temperatures of 1987-2241°K. It was established that the nitride vaporizes with the formation of gaseous titanium and nitrogen

$$TiN_{тв} = Ti_{газ} + {}^1/_2 N_2.$$

The equilibrium constant of this reaction is $K_p = p_{Ti} \cdot p_{N2}^{1/2}$,

From the data of the work it was obtained that

$$\lg K_p = -\frac{41789}{T} - 0{,}60 \cdot 10^{-4} T + 12{,}245,$$

and the partial pressures of titanium and nitrogen of the nitride

$$\lg p_{Ti} = -\frac{27859}{T} - 0{,}40 \cdot 10^{-4} T + 8{,}263,$$

$$\lg p_{N_2} = -\frac{27859}{T} - 0{,}40 \cdot 10^{-4} T + 7{,}963.$$

The heat of the dissociation reaction of ΔH^0_0 was ascertained equal to 191.2 kcal/mole, and the standard heat of formation of titanium nitride ΔH^0_{298} = - 79.4 kcal/mole. (According to [1076] ΔH^0_{298} = 76.76 kcal/mole).

These data were checked by V. V. Fesenko, A. S. Bolgar and E. A. Ryklis, who ascertained that the composition of titanium upon vaporization is noticeably changed, and the vaporization rate from the Knudsen cells depends acutely on the escape area. Therefore the data of work [20 are approximate.

The dependence of the composition of congruent evaporation on temperature (1993-2243°K) is expressed by the equation: $x = 1.46-2.8 \times 10^{-4} T$, where x = N/Ti; the vaporization coefficient of titanium is $\alpha = 1.3 \cdot 10^{-2}$.

Table 54. The vaporization rate of titanium nitride and the dissociation pressure of titanium and nitrogen of the nitride.

Temperature, °K	Vaporization rate $G \cdot 10^6$, g/cm^2·s	Vapor pressure of titanium $p_{Ti} \cdot 10^6$, at	Nitrogen pressure $p_N \cdot 10^6$, at
1987	1,510	1,697	0,650
2017	1,972	2,234	0,854
2050	3,129	3,573	1,366
2155	15,963	18,685	7,146
2212	33,254	39,435	15,08
2241	70,555	84,221	32,2

An investigation of the microhardness of titanium nitride in the region of its homogeneity was carried out in work [147]. It is demonstrated (see Fig. 4) that the concentration dependence of the microhardness is linear and is similar in this respect to the dependence of the microhardness of the titanium and zirconium carbides, [147] and tantalum carbide [148] on the content of bound carbon. However, in spite of the fact that in the latter three cases the extrapolation of the line of microhardness for a carbon content, equal to zero, yields an approximate value of the microhardness of the corresponding metals, this is not observed for titanium nitride. If in the carbides the character of the distribution

of the electron concentration differs little from that for metals, in nitride it varies as a result of the appearance of a considerable fraction of ionic bonding. As can be seen from Fig. 4, the fraction of ionic bonding increases with the reduction in the content of nitrogen in the nitride lattice. The latter can be associated with the formation of Me – Me bonds, by smaller disturbance due to this of the valence electrons of the nitrogen atoms and by a corresponding increase in the energy gap between the d- and s-states of the titanium and the p-state of the nitrogen.

The contractibility of titanium nitride, according to Bridgman [149], is expressed by the following relationships:

$$\Delta V/V_0 = 3{,}32\cdot10^{-7}p - 2{,}13\cdot10^{-12}p^2 \quad \text{when } 30\ ^\circ\text{C},$$

$$\Delta V/V_0 = 3{,}51\cdot10^{-7}p - 2{,}13\cdot10^{-12}p^2 \quad \text{when } 75^\circ\text{C},$$

where V_0 is the volume when p = 0, p is the pressure, kg/cm^2.

The elastic modulus of titanium nitride, obtained on samples with low density (3.03 g/cm^3), is equal to 8060 kg/mm^2 [125, 139], this is an understated value. Then the elastic modulus of titanium nitride was determined equal to 25,600 kg/mm^2 [166]. The elastic modulus of TiN within the limits of temperatures of up to 600°C varies little [195].

According to [1031], the elastic modulus of nonporous titanium nitride is equal to 61,600 $\pm$ 2000 kg/mm^2 (to which the characteristic temperature 796 $\pm$ 15°K corresponds), and according to [1077] is 44,000 kg/mm^2 (Θ = 847°K).

The mechanical properties of titanium nitride have hardly been studied; there exists information only about the limit of its compressive strength at 20°C, which is 100-130 kg/mm^2 [146].

For titanium nitride a low specific electrical resistance is characteristic, equal to about 25 μΩ·cm which is approximately two times lower than the electrical resistance of metallic titanium [144]. An investigation of the electrical properties of titanium nitride in the region of homogeneity, conducted by us jointly with T. S. Verkhoglyadova [145], showed that with a decrease in nitrogen content the fraction of ionic bonding in the lattice is increased with a corresponding variation not only in the level, but also in the nature of the conductivity. The variation in the electrical resistance of titanium nitride in the region of homogeneity (see Fig. 5) is nonlinear and differs from the sequence of resistance of titanium carbide. The appearance of an energy gap in the lattice of titanium nitride with incomplete nitrogen content, assumed for titanium nitride in works [151, 152], is confirmed by measurements of electrical resistance at high temperatures (see Fig. 6). It has been shown that titanium nitride with a nitrogen content, close to stoichiometric (49.8 at. % of N) exhibits a linear increase in electrical resistance with temperature. With a decrease in the nitrogen content to 48.4 at. % a maximum of resistance appears at 1800°C. With further lowering in the nitrogen content the resistance increases with the simultaneous shift of the maximum to the region of lower temperatures: 750°C for the nitride with 43.4 at. % of nitrogen; 550°C for 38.6 at. %. The width of the energy gap with a decrease in the nitrogen content increases. Thus, a reduction in the nitrogen content in titanium nitride within the limits of the region of its homogeneity leads to an increase in the fraction of ionic bonding.

Now the sensitivity of the electricap properties of titanium nitride to impurities is understandable, especially those, which can contribute to an increase in the degree of polarization of the nitrogen atoms. Thus, already in the early work of Münster and Sagel [172] it was demonstrated that the electrical conductivity of films of titanium nitride, applied by condensation from the gaseous phase on various linings, essentially depends on the composition of the latter and the possibility of the transition of its components

in the nitride layer. Nitride films, applied to linings of metallic tungsten, and also of aluminum oxide exhibit a metallic character of conductivity. Nitride films, deposited on a lining of SiO_2, have a negative temperature coefficient of electrical resistance (Fig. 56). This can be connected with the relatively easy reducibility of SiO_2 and the transition in the process of the deposition of the nitride of a definite part of the oxygen of the SiO_2 in the TiN layer, apparently, with the formation of a TiN – TiO solid solution. A subsequent work [174] confirmed these considerations. Data about the electrical properties of films of titanium nitride are given in Table 55.

Table 55. The electrical properties of films of titanium nitride, obtained by the deposition of the gaseous phase on different linings.

Material of the lining	Thickness of the layer of TiN, μ	Specific electrical resistance, Ω·cm		Temperature coefficient of resistance in the interval 700–800°C	Hall constant cm^3/C
		20°C	800°C		
Tungsten	—	$1{,}65\cdot10^{-5}$	$5{,}82\cdot10^{-5}$	$+3{,}2\cdot10^{-2}$	—
Al_2O_3	7	$4{,}6\cdot10^{-5}$	$1{,}2\cdot10^{-4}$	$+2\cdot10^{-2}$	$1{,}2\cdot10^{-4}$
SiO_2	3	$1{,}4\cdot10^{-2}$	$1{,}8\cdot10^{-4}$	$-2\cdot10^{-2}$	—
(quartz)	9	$3{,}9\cdot10^{-4}$	$1{,}6\cdot10^{-4}$	$-4\cdot10^{-4}$	$-1{,}3\cdot10^{-4}$

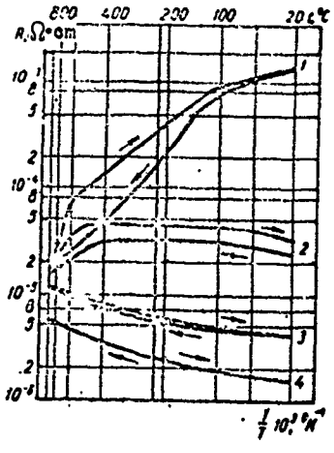


Fig. 56. The temperature dependence of the electrical resistance of films of TiN, applied as linings. 1 – SiO_2 (the thickness of the film is 3 μ). 2 – SiO_2 (the thickness of the film is 9 μ). 3 – Al_2O_3 (the thickness of the film is 7 μ). 4 – tungsten wire.

These data are confirmed by investigations of the electrical properties of the TiN – TiO system, carried out in [174]. It was demonstrated that the addition of oxygen to titanium nitride brings out the semiconductor nature of its conductivity.

In works [1057, 1078] the dependence of the electrical resistance of titanium nitride with the composition $TiN_{0.86}$ on the porosity of the samples was investigated.

With an increase in pressure the electrical resistance of titanium nitride drops, just like for the majority of metals; the mean baric coefficient of electrical resistance at pressures up to 12,000 kg/cm^2 is $9.35 \cdot 10^{-7}$ at 30°C and $9.97 \cdot 10^{-7}$ kg/cm^2 at 75°C [149].

The electrical conductivity of titanium nitride at low temperatures has been repeatedly investigated, where the transition point to superconductivity was assumed within broad ranges – from 1.1 to 5.6°K [168, 169]. The most reliable value of $T_к$ is considered to be 4.85°K [1001].

The thermoemission properties of titanium nitride have been little studied [170]; the work function of the electrons is ϕ = 2.92 eV, Richardson's constant is A = 120 A/cm·deg^2 [140]; according to [252] ϕ = 3.70 eV.

Titanium nitride is slightly paramagnetic with a molar magnetic susceptibility of $48 \cdot 10^{-6}$ [171].[2]

Chemical properties. The first systematic investigation of the resistance of titanium nitride to oxidation was carried out in work [154]. In Fig. 57, according to this work, the dependence of the thickness of the film on a compact sample of TiN obtained by hot pressing on oxidation time at various temperatures is shown. On the basis of chemical and electron diffraction analysis of oxide films it was established that even at low temperatures a solid thin layer of TiN – TiO solid solution will be formed on the nitride,

similar to the pseudomorphic layers, observed in the oxidation of metals. Upon achieving a definite critical thickness this layer in its external part begins to be converted into Ti_2O_3 and TiO_2. The first stage – the formation of a layer of TiN – TiO solid solution – corresponds to the initial section of isotherms (curvilinear), and the second stage – the rectilinear section. The diffusion of oxygen ions through the layer of the TiN – TiO solid solution is connected with considerable apparent activation energy, constituting, according to work [154], 54.94 kcal/mole.

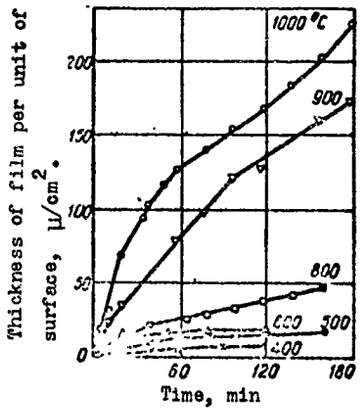


Fig. 57. The dependence of the thickness of a film on a sample of TiN on oxidation time at different temperatures.

In work [238] was conducted a study of the oxidation of titanium nitride (the specific surface is 1500 g/cm^2) powder dispersed in dry and humid air at 600-750°C. The basic conclusions of work [154] were confirmed; it was shown that the oxidation curves consist of two sections – an initial rectilinear one, corresponding to the chemical interaction of titanium nitride with oxygen, and a subsequent one – a nonlinear one, corresponding to the diffusion of oxygen to the titanium nitride through the oxide film. It was ascertained that the oxidation curves of the nitride in humid air (to 6 vol. % of water vapors) practically coincide with oxidation curves in dry air that indicates in principle an identical oxidation mechanism. The activation energy for the first oxidation stage (the chemical interaction of the nitride with oxygen) is 44.9 kcal/mole, for the second stage (diffusion through the oxide film) – 54.60 kcal/mole which agrees well with the data of [154] – 54.94 and [239] – 54.30 kcal/mole.

Technically noticeable oxidation of titanium nitride begins at temperatures higher than 700-800°C. According to [238], titanium nitride powder at 850°C is completely oxidized in less than 10 min.

A further detailed investigation of the kinetics and the oxidation mechanism of titanium nitride was carried out by Münster and Schlamp [155], who also analyzed the data of the corresponding works of other researchers. The authors [155] investigated the oxidation rate of titanium nitride in the temperature interval of 625-1075°C in pure oxygen with its normal pressure on the titanium nitride samples, deposited in the form of layers on alundum plates (according to the reaction $TiCl_4 + 2H_2 + 1/2\ N_2 \rightarrow TiN + 4HCl$; the nitrogen content in a layer was 22.2-22.9%). The shapes of the isotherms, obtained in this work, were analogous to the isotherms in Fig. 57, i.e., they also consist of two sections – a parabolic and a linear one to which the activation energies respectively correspond 46,400 and 24,500 cal/mole. In the accepted limits temperatures the isotherms are satisfactorily described by the equation $t = ay^2 + by$; above 900°C with protracted periods of oxidation certain deviations occur.

Münster and Ruppert [157] ascertained that the surface layer of titanium nitride with a thickness of less than 1 μ is completely destroyed in air within several hours at 700°C. Pollard and Woodwart [158] studied the interaction of titanium nitride with oxygen at 1000°C with respect to the variation in pressure in the system. In the first 15 min the pressure drops sharply (by approximately two times), then a slow increase in the last begins. An analysis of the residual gas showed that the atomic ratio of absorbed oxygen to liberated nitrogen was equal to 1.7, whereas for the reaction

$$TiN + O_2 = TiO_2 + {}^1/_2N_2$$

the ratio expected, was equal to 2. The pressure drop in the initial period was explained by the slow elimination of nitrogen from the lattice, and the noncorrespondence of the amounts of absorbed oxygen and liberated nitrogen – by the dissolution of oxygen by the nitride lattice. Basically these observations agree with the data of work

[154] with respect to the formation upon oxidation of titanium nitride in the initial period of the layer of the TiN – TiO solid solution. In work [159] the exaggerated border of stability of compact titanium nitride to oxidation is cited, corresponding to 1100-1400°C.

Powered titanium nitride burns in a stream of oxygen even at 700-800°C.

With respect to hydrogen stoichiometric titanium nitride is inert. Thus, according to [110], the nitride baked to the melting point preserves in a hydrogen medium its complete nitrogen content; authors of certain early works observed only slight absorption of hydrogen upon the heating of nonstoichiometric nitride at 1000°C, and also a very insignificant liberation of ammonia under similar conditions [139]. Mixtures of nitrogen and hydrogen do not interact with titanium nitride at 1200°C [158].

Titanium nitride of stoichiometric composition is stable with respect to the action of CO; a nitride with a nitrogen deficiency is readily decomposed by CO and CO_2. The oxidation of stoichiometric TiN by carbon dioxide proceeds slowly according to the reaction

$$2TiN + 4CO_2 \rightarrow 2TiO_2 + 4CO + N_2,$$

the rate constant of which is expressed by an equation for reactions of the second order [158]

$$K = \frac{4\Delta p}{p\tau(p - 4\Delta p)},$$

where p is the initial pressure of the CO_2, Δp is the variation in pressure during the time τ of the reaction (Table 56).

Water vapors practically do not act on the titanium nitride; an attempt at the beginning of the 1900's to use titanium nitride to produce ammonia by the action on it of mixtures of H_2O vapor and oxygen under reduced pressure did not give positive results [139].

Table 56. The rate constants of the oxidation of titanium nitride with carbon dioxide.

τ, min	p, mm Hg	K_p, mm Hg^{-1} min^{-1}	τ, min	p, mm Hg	K_p, mm Hg^{-1} min^{-1}
0	2,75	0,021	50	3,18	0,013
10	3,00	0,021	60	3,22	0,013
20	3,08	0,013	70	3,24	0,013
30	3,11	0,012	80	9,26	0,013
40	3,14	0,012	90	3,28	0,014

At low temperatures (up to 270°C) chlorine does not act on titanium nitride, and at temperatures from 300 to 400°C TiN is chloridized by gaseous chlorine [160]. Upon heating in a stream of HCl at 600-650°C titanium nitride is quantitatively converted to $TiCl_4$ [161].[3]

Titanium nitride is decomposed by HCl (at temperatures higher than 1200-1300°C) with the formation of a mixture of gaseous $TiCl_4$ with hydrogen and nitrogen. Along with $TiCl_4$ the lower chlorides of titanium $TiCl_3$ and $TiCl_2$ will also be formed. This mixture is able to act on metallic surfaces (for example, on molybdenum) with the formation of titanium nitride again [237].

Titanium nitride energetically reacts with NO and NO_2, however a quantitative investigation has still not been carried out [158].

Upon heating titanium nitride in a stream of hydrogen with sulfur vapors introduced into the latter at a temperature of 700-800°C the nitride is converted into titanium sulfide [139].

The behavior of titanium nitride with respect to acids and alkalis has been investigated in great detail in recent years [162]. The TiN during the course of 24 h at room temperature practically does not dissolve in hydrochloric, sulfuric, perchloric, phosphoric acids or mixtures of perchloric and hydrochloric, oxalic and sulfuric acids.

Boiling hydrochloric sulfuric and perchloric acids act weakly on it within 2 h; it is unstable in the cold to the action of sodium hydroxide solutions. A survey of the early works concerning this question is given in [139].

Refractory properties [163, 164]. Titanium nitride is resistant to the action of molten tin, bismuth, lead, cadmium and zinc (Table 57).

Table 57. The behavior of titanium nitride in contact with molten metals.

Metal	Temperature °C	Time of contact, h	Content of Ti in the metal after remelting, %
Sn	350	10	Not detected
	350	40	0,26
Bi	380	10	Traces
	380	40	0,07
Pb	450	10	0,04
	450	40	0,20
Cd	450	10	0,20
	450	40	0,07
Zn	520	10	0,06

Molten pig iron and basic cupola slag at a temperature of 1500°C moisten titanium nitride, but do not react with it. Chekh and Seybal in the Institute of Powder Metallurgy ChSSR investigated the wettability of titanium nitride in a vacuum at 1550°C. It was found that titanium nitride does not moisten iron; it moistens nickel well; nickel and chromium alloy (1:1) is corroded by the nitride. Under the effect of molten aluminum slight surface corrosion of titanium nitride (after 30 min 1000°C).

A crucible of titanium nitride (20.75% N), baked at 1800°C in a vacuum at a pressure of 1.5 mm Hg for 15-30 min, was not corroded and was not destroyed in molten electrolytic iron (at 1700°C), raw iron (1600°C), nickel, cobalt, chromium (1600°C), manganese (1400°C), copper (1200°C), aluminum (1000°C) and iron

phosphide (1200°C) [139]. Very pure titanium nitride also does not react with iron in vacuum.

With intense heating the nitride does not react with tungsten powder; the addition of up to 10% TiN to tungsten hardly varies the melting point of the latter; with a further increase in the nitride content of the melting point drops, however it was not metallographically possible to observe a reaction. Thus, according to work [110], titanium nitride does not react with tungsten in a broad region of temperatures and compositions. It was noted that a tungsten filament does not react with titanium nitride also when producing the latter by the method of accumulation from the gaseous phase.

Crucibles of titanium nitride at high temperature are intensely corroded by the oxides Fe_2O_3, MnO, SiO_2 and glass [164]. Powdered titanium nitride is oxidized upon heating with readily reducible oxides of the CuO, PbO, HgO type, where oxidation is frequently accompanied by intense sparking and spontaneous combustion.

The authors [165] investigated the electrochemical behavior of anodes of titanium nitride in a LiCl + KCl chloride melt and showed that even at low current densities (D_a = 0.004-0.035 A/cm^2) prolonged electrolysis is accompanied by the liberation on them of nitrogen and by the transition of tetravalent titanium in the electrolyte. Below $1.5 \cdot 10^{-3}$ A/cm^2 the anode potential varies little with current density; a considerable polarization of the nitride anodes is observed in the interval 0.002-0.2 A/cm^2, where the potential increases by 0.6-0.7 V. Above 0.2 A/cm^2 the anode potential practically becomes constant.

The results of the study of the behavior of titanium nitride in contact with niobium, tantalum, molybdenum and tungsten in the solid state at temperatures of 1600-2100°C, conducted by us jointly with G. A. Yasinskaya and E. A. Pugach according to the method, described in work [163], show that titanium nitride is most stable in contact with molybdenum (Table 58).

Table 58. The behavior of titanium nitride in contact with refractory metals at high temperature.

Temperature, °C	Nb		Ta		Mo		W	
	2 h	5 h	2 h	5 h	2 h	5 h	2 h	5 h
1600	—	—	н	—	н	—	н	—
1800	—	сл	—	н	н	н	н	н
2000	в	в	в	—	сл	сл	сл	в
2100	с	с	—	с	—	в	в	—

Note: в – react, с – react intensely, сл – react slightly, н – do not react.

The interaction of titanium nitride with carbon was investigated in [157]; it was found that the reaction

$$TiN + C \rightleftarrows TiC + {}^1/_2N_2$$

is accompanied by a decrease in free energy, being dependent upon temperature

$$\Delta F^0 = 39650 - 20{,}15T \quad \text{(Fig. 58, line 1).}$$

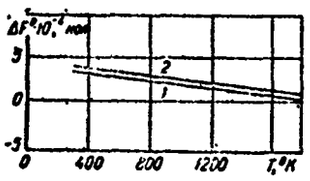


Fig. 58. Variation in free energy upon the carburization of titanium nitride. 1 – according to the reaction $TiN+C \rightleftarrows TiC+{}^1/_2N_2$; 2 – the same, but taking into account the formation of the solid solutions TiC–TiN (x_{TiC} = 0.7).

Thus, with an increase in temperature the resistance of the nitride with respect to carbon decreases, obviously, due to its inclination to dissociate, and carbide will be partially formed. This equation for ΔF^0 is derived neglecting the formation of solid solutions of TiN – TiC; if one were to consider the latter, then the variation in free energy would be expressed by the equation

$$\Delta F^{\circ}_{TiN-TiC} = {}^{1}/_{2}RT\ln p_{N_2} = RT\ln\frac{x_{TiC}}{x_{TiN}} + RT\ln\frac{f_{TiC}}{f_{TiN}},$$

where x is the molar concentration, f is the coefficient of activity. Line 2 in Fig. 58 shows the variation in free energy upon the formation of the solid solutions, $x_{TiC} = 0.7$, where it is assumed that $f_{TiC} = f_{TiN} = 1$. As can be seen, the formation of the solid solution TiN – TiC has little effect on the reaction of titanium nitride with carbon.

In [231, 232, 1079] the interaction reaction of titanium nitride with carbon ($TiN + C = TiC + \frac{1}{2}N_2$) within the temperature limits of 1480-2480°C was again investigated at the atmospheric pressure of nitrogen. The expression for the temperature dependence of the equilibrium constant was found

$$\lg K_p = -\frac{5600}{T} + 2{,}78,$$

and it was also shown that the limiting link in determining the equilibrium state are the diffusion processes – the supply of carbon to the surface of the titanium nitride particles, and also diffusion inside the particles.

Methods of producing titanium nitride. The basic methods of producing titanium nitride are:

1) the nitridation of metallic titanium or its hydride;

2) the interaction in the gasecus phase between $TiCl_4$ and ammonia or mixtures of nitrogen and hydrogen;

3) the decomposition of titanium amminochlorides and other similar compound, containing titanium and nitrogen;

4) the reduction of TiO_2 with carbon or metals in a nitrogen medium.

The nitridation of metallic titanium was first carried out by Liebig in 1831. In works [175, 141, 143] titanium nitride was produced by the nitridation of titanium powder in molybdenum boats at a temperature of 1100-1200°C in nitrogen or in a stream of $H_2 + N_2$ in a pocelain tube in 1-2 h. Alexander [176] proposed producing titanium nitride by nitriding its hydride; this method was used by Duwey and Odell [177], who nitrided the hydride at 1800-1900°C with pure nitrogen. An analogous method was developed by Foster [196], who nitrided titanium hydride by heating it in a stream of NH_3 for almost 100 h at 1000°C. Ehrlish [135] produced titanium nitride by nitriding 99.9% titanium shavings with pure nitrogen for 2-3 h at 1200°C (in a corundum tube). And after a single nitridation a nitride of the composition $TiN_{0.95}$ will be formed. After the pulverization and repeated nitridation of this product the nitrogen content increases to $TiN_{1.00}$, i.e., to the expected 50 at. %. By heating a mixture of TiN + Ti in a tungsten boat, Ehrlish [135] produced titanium alloys with a broad range of nitrogen content of the latter with arbitrary formulas from $TiN_{0.1}$ to $TiN_{1.0}$.

Gvozdov and Zhurenkova [204], who also investigated the reaction of titanium with nitrogen, ascertained that up to 500°C nitrogen does not act on titanium; absorption begins at 500°C and at 800°C energetically develops with the formation of titanium nitride. It was noted that the absorption of nitrogen by titanium sharply reduces the subsequent absorption of hydrogen, and this reduction more significant than in the case of preliminary oxidation of titanium.

The process of the nitridation of powdered titanium under conditions, practically eliminating simultaneous oxidation, was investigated in detail in [178].

For the nitridation titanium powder with a purity of 99.98% (lattice constant a = 2.96; c = 5.64 Å) was used, the nitridation temperature was varied from 500 to 1200°C, and the exposure at each temperature was from 15 to 240 min. The temperature dependence of the rate of speed nitridation is given in Table 28. The results of

the nitridation of pure titanium powder (Fig. 59) show that the dependence of the nitrogen content at temperatures of 700-900°C obeys to the linear, and above – the parabolic law of saturation, which one should have expected, considering the broad region of homogeneity of titanium nitride and the complication of the process of nitrogen diffusion into the crystal lattice in proportion to the filling of the pores between the metallic atoms and the approach to the upper border of the region of homogeneity. The main saturation of titanium with nitrogen occurs in the first 10-15 min, and with subsequent exposure the nitrogen content increases insignificantly. The complete termination of reaction diffusion with the formation of a nitride of saturated composition is attained with an exposure of 2-4 h at 1200°C. The experiments with the nitriding of hydrogenated titanium (with 99.2% Ti), carried out in that same work, showed that the hydrogen, introduced into the titanium lattice, severely inhibits the diffusion of nitrogen at relatively low temperatures of the order of 500-800°C, when titanium hydride is sufficiently stable. Other things being equal the products of nitridation contain two times less nitrogen. Starting at 1000°C, when titanium hydride noticeably dissociates, the saturation by nitrogen occurs more intensively, and the maximum saturation by nitrogen is attained at 1200°C in the course of 2-4 h, i.e., under those same conditions, as for the original pure titanium powder. With the nitridation of titanium powder with ammonia (Fig. 60) the diffusion of nitrogen is inhibited.

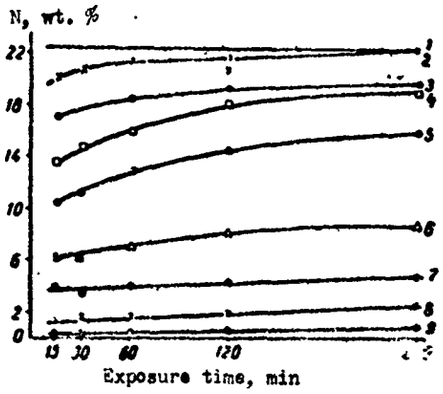


Fig. 59. The dependence of the nitrogen content in titanium powder, nitridation at 500--1200°C on the exposure time. 1 – theoretical content; 2 – 1200; 3 – 1100; 4 – 1000; 5 – 900; 6 - 800; 7 - 700; 8 - 600; 9 - 500°C.

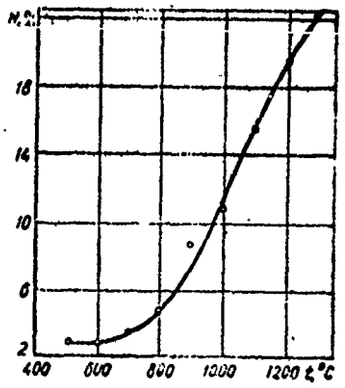


Fig. 60. The temperature dependence of the nitrogen content in titanium upon its treatment with ammonia.

The nitridation of titanium hydride ($TiH_{1.94}$) within the temperature limits of 700-1300°C showed that stoichiometric TiN can be produced within 5 h at 1300°C [1000].

Researchers [226] prepared titanium nitride by the nitridation of titanium powder (99.5 %) produced by the reduction of TiO_2 with calcium hydride. The nitridation was carried in a TVV-2 furnace with well purified nitrogen under the following conditions: blowing hydrogen through the furnace for 20 min, blowing nitrogen through the furnace nitrogen for 20 min, heating for 1 h up to 1200°C, exposure in a stream of nitrogen at 1200-1250°C for 2.5 h, cooling with the furnace. The titanium nitride produced under these conditions contained 77.35% Ti and 22.39% N, i.e., it was close to stoichiometric composition.

Gulbransen and Andrew [179], who studied the nitridation rate of titanium at a pressure of 769 mm Hg with the formation of titanium nitride according to the simplified reaction[4] $Ti + 1/2\ N_2 = TiN$, determined the character of the dependence of the rate of constant on temperature (Fig. 61) and time (Fig. 62) of nitridation at 500--900°C. For the temperature dependence of the rate constant of the nitration reaction there were obtained:

Temperature, °C	K, $g/cm^3 \cdot s$	Temperature, °C	K, $g/cm^3 \cdot s$
550	$5{,}28 \cdot 10^{-15}$	775	$1{,}08 \cdot 10^{-12}$
600	$2{,}97 \cdot 10^{-14}$	800	$1{,}46 \cdot 10^{-12}$
700	$2{,}78 \cdot 10^{-13}$	880	$3{,}2 \cdot 10^{-12}$

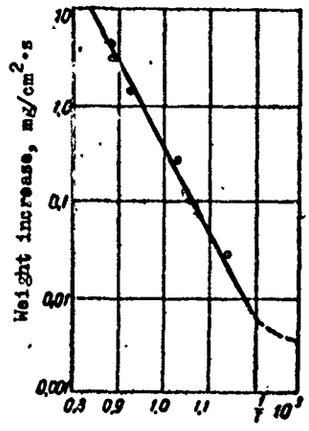


Fig. 61. The temperature dependence of the rate constant of the reaction of Ti + 1/2 N_2 on temperature.

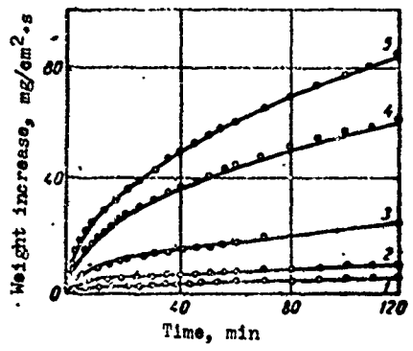


Fig. 62. The dependence of the weight increase due to the nitridation of titanium on time. 1 – 500; 2 – 600; 3 – 700; 4 – 800; 5 – 900°C.

The heat of activation calculated from these data upon the diffusion of nitrogen into the titanium with the formation of titanium nitride was equal to 36,300 cal/mole. The time dependence of the weight increase as a result of the nitridation is expressed by the empirical equation

$$W^2 = K\tau,$$

where W is the weight increase, mg/cm^2 of surface of sheet titanium (99%), K is a constant, τ is the nitridation time. The nitridation titanium iodide of high purity proceeds much slower.

The variation in pressure within the limits of 76-760 mm Hg has little effect on the nitridation rate which is explained by the formation of a nitride film on the titanium, the dissolution rate of which in the metal determines the rate of the nitridation reaction.

Richardson and Grant [180] investigated the interaction of nitrogen with titanium in the region of higher temperatures – from 700 to 1050°C. They used technical titanium which was nitrided at initial nitrogen pressures of 0.2-0.5 at. The nitridation rate was approximately 50 times less than the oxidation rate of titanium. In the surface films on the nitridation titanium only the presence of the nitride TiN was established.

The addition to the titanium powder of 5% KHF_2 as a catalyst substantially accelerates the nitridation process [246].

One of the technological procedures for producing titanium nitride is with titanium melt in a nitrogen medium, which was first time proposed for this purpose by V. P. Remin [181]. Subsequently, the regimes of this procedure were developed in the work [132]: the melting of titanium was carried out by a current 150 A, then the current intensity was increased to 300 A; the material was held at both values of current intensity for 2-3 min. A deficiency of this procedure is the significant liquation of nitrogen which hampers the producing of a uniform product.

The authors [306] take note of the fact that the phases forming upon nitridation of refractory metals, in particular of titanium, are sufficiently refractory which inhibits the diffusion through them nitrogen, impedes, and in certain cases makes practically impossible the technological execution of nitridation. Therefore, it is recommended in proportion to the saturation of the sample with nitrogen to increase the nitridation temperature in order to increase the mobility of nitrogen in the surface layer of the metal being nitrided.

<u>The interaction in the gaseous phase between $TiCl_4$ and ammonia or mixtures of nitrogen and hydrogen</u>. The method of producing tianium nitride by the interaction between $TiCl_4$ and ammonia is one of the oldest methods of producing this nitride, proposed by many researchers, starting with Veler and Sainte-Claire DeVille [1858 [139]). At the basis of this method lies the reaction

$$2\,TiCl_4 + 2\,NH_3 = 2\,TiN + 6\,HCl + Cl_2,$$

which is carried out at temperatures higher than 1000°C, i.e., the titanium tetrachloride is practically reduced by a mixture of hydrogen with nitrogen. The technological development of this method is given in detail in the patent [182] for producing finely dispersed and homogeneous (with respect to chemical composition) titanium nitride. The essence of the technology consists in the supply of ammonia and titanium tetrachloride preheated to a temperature of 700-900°C into a quartz reaction chamber through an injector, along an internal channel of which the tetrachloride moves, and along an external annular space – the ammonia. The reaction temperature in the chamber is maintained within the limits of 750-950°C; for each mole of titanium tetrachloride in the gaseous phase 2-4 moles of ammonia are necessary; the rate of the passage of the gases into the reaction chamber is from 2 to 20 m/s. It was demonstrated that the best results were obtained with the laminar flows of gases, for which the intake of the latter into the reaction chamber is accomplished by a large number of injectors with a diameter of the internal tube of 0.5-8 mm. The reaction temperature immediately near an injector exit should be 100-1200°C that ensures a sufficiently high completeness of the reaction:

Temperature, °C	800	1000	1200
Degree of conversion into nitride, %	75,6	95,7	99,6

The product, coming out of the reaction chamber consists of a very fine nitride suspension in a gaseous medium of chlorine, HCl vapors, unreacted reagents, admixtures of other gases, which could pass through with the feeding of reagents into the chamber.

This mixture is first cooled in tubular heat exchangers, and then the titanium nitride will be separated in a cycline separator by electrostatic precipitation or filtration by a ceramic filter.

The titanium nitride produced by described method is a powder with particle dimensions of 0.1-0.6 μ with a nitrogen content of 22.2-22.6%.

According to [185], titanium nitride can also be obtained by the interaction titanium tetrachloride with ammonia. It was determined that below 1400°C a nitride will be formed, in the lattice of which are 15-20% vacant titanium points, which does not agree with the above-cited data.

A variant of this method consists in the accumulation from the gaseous phase of titanium nitride on a metallic filament usually according to the reaction

$$2\,TiCl_4 + N_2 + 4\,H_2 = 2\,TiN + 8\,HCl.$$

Van Arkel [183] produced titanium nitride by this method on a tungsten filament, heated to 1400-2000°C, where the deposition consisted of large single-crystal formations. Analogous works were carried out by Moers [184], and also by Campbell with his colleagues [159], who investigated in detail the effect of temperatures, pressures, and current on the process of accumulating the nitride from the gaseous phase. In work [158] it was indicated that titanium nitride, exactly responding to the formula TiN, will be formed by the deposition method from the gaseous phase on a wire, heated to ~1450°C, with a total pressure in the reaction chamber of 300-400 mm Hg, with a partial pressure of $TiCl_4$ of 17 mm Hg and a content ratio of $N_2:H_2$ = 1:1.

In the recently completed work [1050] crystalline titanium nitride was produced by an analogous method: by deposition on a tungsten rod. At a temperature of 1400°C and a Ti:N ratio in the gaseous phase, equal to 1:4 conditions are created for growing crystals with dimensions of 3 × 3 mm; the nitrogen content in them is 21.0-21.3% ($TiN_{0.9}$).

The decomposition of titanium amminochlorides. The most detailed investigation of this oldest method of producing titanium nitride was carried out by A. Kh. Breger. In work [186] Breger production of titanium nitride by the reaction in the gaseous phase between $TiCl_4$ and NH_3 at 800°C above inert substances with subsequent heating at 300-350°C of the obtained intermediate product $Ti/NH_2/Cl_2 \times$ $\times 2NH_4Cl$ to amminochloride $TiCl_4 \cdot nNH_3$ (where n = 4, 6, 8) at high temperature with decomposition according to a reaction of the type

$$TiCl_4 \cdot 4NH_3 \rightarrow TiN + HCl + NH_3.$$

The decomposition of $TiCl_4 \cdot 4NH_3$ at low temperatures of the order of 400-800°C leads to the formation of compounds of titanium with nitrogen, containing a deficiency of titanium (and an excess of nitrogen corresponding to the formula $TiN-Ti_xN$, where x = 0.85-0.95). With an increase in the heat-treating temperature of the amminochlorides the composition even more approaches the formula TiN, attaining it at 1400-1600°C.

With the use for producing titanium nitride of amminochloride $TiCl_4 \cdot 6NH_3$ a significant part of the latter vaporizes, and the yield of titanium nitride is not more than 8-10% after 6 h of heat treatment at 1500°C [187].

It is assumed that the amminochlorides are not decomposed at once to titanium nitride, but with the formation of the intermediate compound TiNCl (a compound of black color with a tetragonal structure), forming at 350-400°C. Upon the heating of this intermediate product for 6-8 h at 400°C a cubic product with a TiN-lattice is produced, but still containing chlorine atoms, for the complete removal of which from the lattice heating to 1000°C is necessary [188]. Thus, the production of titanium nitride with amminochlorides can be on the whole represented in the following manner:

$$TiCl_4 + NH_3 \rightarrow Ti(NH_2)Cl_2 \cdot 2NH_4Cl \xrightarrow{300-350^\circ C}$$

$$\rightarrow TiCl_4 \cdot nNH_3 \xrightarrow{400\ C} TiClN \xrightarrow{< 1000^\circ C} TiN.$$

The reduction of TiO_2 with carbon or metals in a nitrogen medium. The production of titanium nitride by the reduction of TiO_2 with carbon in a nitrogen medium is based on the reaction

$$TiO_2 + 2C + \tfrac{1}{2}N_2 = TiN + 2CO$$

and consists in the reduction of TiO_2 with carbon to titanium or its lowest oxides with their simultaneous nitridation to nitride or hydroxy-nitrides. In the work of Friederich and Sittig [110] TiO_2 or rutile heated in a mixture with pine black (1% ashes) in a tungsten, molybdenum or carbon boat in a current of nitrogen for several hours at 1250°C. The formation hydroxy-nitrides in this investigation was not observed and the reaction product contained 98-99.5% titanium nitride (a nitrogen content of the order of 21.9%) [110, 167].

Ruff and Eisner [187] also prepared titanium nitride by heat treating a mixture of titanium dioxide with carbon black in a stream of nitrogen at 1100-1200°C and showed that the product corresponds in composition to the formula TiN.

Subsequently Remin [181] subjected a mixture of titanium dioxide to nitridation with activated carbon, consisting of a weight ratio of 2:1 (i.e., with a carbon content smaller than is expected from the above-cited reaction). Nitridation was carried out carefully with purified nitrogen, ammonia and a mixture of nitrogen with hydrogen, in which the charge was placed in an iron, nickel or porcelain boat. As a result it was ascertained that in triple nitridation with ammonia (each time for 3 h at 1250°C) the nitrogen content in the obtained product is 17.61%; with the same treatment with nitrogen 17.47%, and with nitridation with a mixture of $N_2 + H_2$ as a result of a 6-hour operation (the temperature rise to 1250°C lasts about 3 h and the exposure at this temperature is also for 3 h) the nitrogen content reaches a total of 16.4%. In this work by additional nitridation it was not possible to increase the nitrogen content in the nitride.

By the indicated method the formation of titanium nitride, obviously, is possible only after the stage of the formation of the lowest oxides of titanium, in the first place of titanium oxide TiO, which forms a continuous series of solid solutions with titanium carbide formed as a side reaction according to the scheme:

$$TiO_2 + C = TiO + CO,$$
$$TiO_2 + 3C = TiC + 2CO,$$
$$TiO + TiC = TiO - TiC.$$

Upon nitridation of the solid solution a ternary solid solution TiO-TiC-TiN will first be formed, from which titanium nitride is subsequently obtained

$$TiO - TiC - TiN + N_2 = 3TiN + CO.$$

This reaction scheme is confirmed by the data of the work of Belyakova, Komar and Mikhaylov [191], according to with the nitride produced by the nitridation of a mixture of TiO_2 with carbon at a temperature of 1100-1500°C, and also titanium carbide are dissolved in TiO, so that the solid solutions TiN-TiC-TiO are produced; upon carrying out the reaction at 1900°C for 3 h the titanium oxide is completely reduced and the solid solution TiN-TiC will be formed, the concentration of which is determined by relationships, established in the work of Zelikman and Gorovits (see below). In the same work [191] by attempting the direct nitridation of TiO_2 with a mixture of $N_2 + H_2$ it was established that at temperatures of 1000-1500°C formation of intermediate titanium oxides occurs, and at 1700°C the solid solution TiN-TiO will be formed.

Other reaction patterns are also possible, for example, those cited in monograph [146], however the most important of the side reactions under all circumstances is the formation of carbide titanium, yielding stable solid solutions with titanium nitride. With the sintering of cermet solid alloys the nitrogen, located in

their composition in the form of the solid solution TiN-TiC, is practically not liberated from the alloy, remaining in the carbide solid solution [189]. Up to a temperature of 1200°C the oxidizing action of the air being sucked into the furnace mainly appears, i.e., the formation of hydroxy-nitrides is taking place, and in the temperature range of 1200-1800°C the nitriding action predominates.

Thus of great importance for the production of titanium nitride by the reduction of titanium dioxide with carbon in a nitrogen medium is the work of Zelikman and Gorovits [190] studying the equilibrium of TiC-TiN during the action of nitrogen on the titanium carbide

$$x\mathrm{TiC} + y/2\mathrm{N_2} \rightleftarrows \mathrm{TiN}_x[(x-y)\mathrm{C}, y\mathrm{N}] + y\mathrm{C}.$$

The constant of this reaction [190] was defined as: $K_p = p_{N_2} \cdot \frac{(\mathrm{TiC})}{(\mathrm{TiN})}$ and it was found that at a nitrogen pressure of 0.12 at. (90 mm Hg) depending on temperature it is: at 1300°C – 0.14, at 1500°C – 0.22 and at 1800°C – 0.36. On the basis of these data for P_{N2} = 0.12 at. the reaction isochore equation was derived

$$\lg K_p = -\frac{2700}{T} + 0{,}85.$$

In work [231], however, it was shown that in writing the equation of the reaction constant the authors [190] permitted an error and it is necessary to write it in this form

$$K_p = \sqrt{p_{N_2}}\,\frac{(\mathrm{TiC})}{(\mathrm{TiN})},$$

which brings about good coordination with the experimental data of work [190].

It follows from this that nitrogen saturation at a given pressure decreases with an increase in temperature. Thus, for producing carbon-free titanium nitride with normal nitrogen pressure in a furnace, equal to 1 at. it is necessary to carry out the nitridation at temperatures not higher than 1000-1300°C, and at higher temperatures for complete nitridation of TiC the nitrogen pressure should exceed 1 at.

These data were confirmed by experimental work, conducted by us jointly with V. S. Neshpor on the nitridation of a mixture of TiO_2 with carbon black in a current of nitrogen in a tubular-graphite furnace [146]. It was found that nitridation begins at 1000°C; with a one-hour exposure the nitride yield is a total of 6-7%; at 1300°C the yield increases to 15-20%; at 1400°C the yield sharply increases to 65-70% and at 1600°C it reaches 93-94%. With the subsequent increase in temperature up to 1700°C yield drops to 77-78% with a simultaneous increase in the nitridation product of titanium carbide due to the shift of the equilibrium in the direction of the formation of TiC which agrees well with the data of [190]. The greatest nitrogen content in the nitridation product (at 1600°C) is 21-22%. An increase in the exposure time at this temperature does not lead to any noticeable change in the nitrogen content.

Positive results in carrying out the nitridation process at relatively low temperatures (of the order of 1200°C) are given by multiple nitridation of the triturated intermediate products. Thus, in our work with V. S. Neshpor the nitrogen content after the first nitridation was 12.5% at 1200°C after trituration (to destroy the nitride films on the oxide particles) and after repeated nitridation – 18.5% and after the next trituration and third nitridation – 20.06%. The coarseness of the nitride grains with this remains practically constant and equal to 2-3 μm.

One of the variants of the technology of producing titanium nitride by the reduction of its oxygen compounds with carbon with simultaneous nitridation is the method of the formation of

nitride powder, proposed in work [194], consisting in the nitridation of a mixture of TiP_2O_7 (produced by the action of $H_4P_2O_7$ on $Ti(OH)_4$, taken in the hydrolysis in the process of producing TiO_2 and having particle dimensions of 0.05-0.2 μm) with carbon in a stoichiometric ratio, which is carried out at 1500-1600°C in a nitrogen medium. As a result titanium nitride is obtained in the form of a powder with particle dimensions of 1-50 μm.

Summarizing what has been said, it is necessary to note that the method of nitriding mixtures of TiO_2 with carbon is unsuitable for the production of pure nitride, but is very convenient and technological for the preparation of large quantities of titanium nitride of technical quality for use, for example, in the composition of refractory materials and other articles, not requiring nitride of high purity.

Alexander [192] proposed an analogous method of producing titanium nitride with only one difference, that the reducing agent of the dioxide is not carbon but calcium hydride CaH_2. A mixture of fine TiO_2 powder with a small excess of the hydride to a calculated quantity according to the reaction equation

$$TiO_2 + CaH_2 = Ti + H_2O + CaO$$

was placed in a furnace and heated to form titanium in an inert gas atmosphere, after which nitrogen or ammonia is introduced into the furnace for the formation of titanium nitride

$$Ti + N_2(NH_3) \rightarrow TiN + (H_2).$$

After washing the nitridation product of calcium oxide very pure titanium is produced by this method.

In the opinion of Alexander, the use of calcium hydride to reduce titanium oxide provides a very active reduction as a result of the dissociation of the hydride with the formation of atomic hydrogen. However this opinion was disproved by the experiments of Meyerson and Kolchin [193], who demonstrated that the recombination time of atomic hydrogen into H_2 is so short that it is not able to participate in the atomic state in the reduction process, which is carried out by the calcium. The hydrogen liberated upon dissociation of the hydride serves as the basis of a protective medium, preventing the oxidation of the titanium.

Analogous experiments were conducted by us jointly with G. Z. Lankina using magnesium as a reducing agent of TiO_2

$$2TiO_2 + 4Mg + N_2 = 2TiN + 4MgO,$$

however even at reduction temperatures of 1400-1600°C they did not yield a nitrogen content in the nitration products higher than 7-8% with a titanium content of 72-73%, i.e., the nitridation products are titanium hydroxy-nitrides.

Upon the action of ammonia on TiO_2 at a temperature of 900°C mixtures of titanium nitride (a = 4.242 Å) will be formed with the lowest oxides and hydroxy-nitrides [252].

Sintering of titanium nitride. To produce dense articles of titanium nitride it is most effective to use the method of hot pressing of its powder, which is carried out at 1900-2100°C under a pressure of 200-300 kg/cm^2 [232]. The minimum residual porosity of samples sintered by hot pressing is 2-4%. Upon the sintering of titanium nitride powder acute enlargement of the particles (from 2-3 to 16-18 μm) occurs and intense embrittlement, not characteristic of other nitrides (for example, upon the sintering of tantalum nitride the coarseness of particles increases from 4 to 6-7 μm). In Fig. 63 the microstructure of sintered titanium nitride is shown.

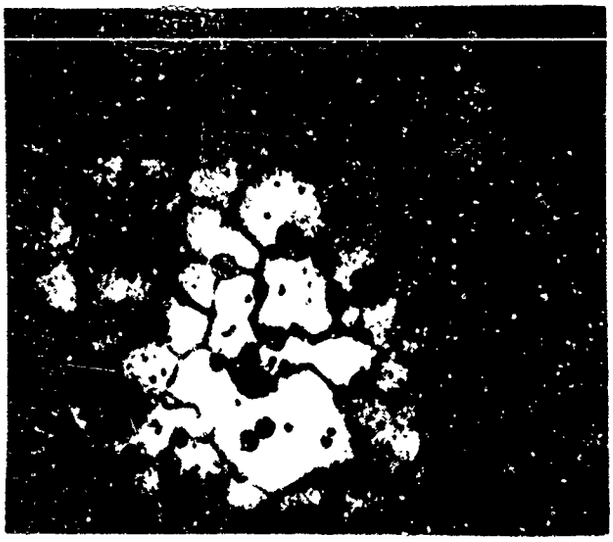


Fig. 63. The microstructure of sintered titanium nitride.

Upon the sintering of briquets, pressed from titanium nitride powder in a vacuum, the porosity of the articles, sintered at a temperature of 2200°C for 4 h, is 22% [232].

The original method of preparing articles of titanium nitride was reaction sintering, consisting in the simultaneous formation of titanium nitride from the metal and sintering, and carried out by sintering of the intermediate products, pressed from titanium powder in a nitrogen medium. This method was simultaneously proposed in 1963 by Samsonov and Verkhoglyadova [233, 225], Gooding and Perratt [234]. Since in the formation of titanium nitride from the metal an increase in specific volume (by 7.5%) occurs, with reaction sintering this increase is realized by reducing the overall porosity of the intermediate product of titanium which makes it possible, according to work [235], to produce articles of titanium nitride with a porosity of 13% (samples of titanium hydride were used), pressed under a pressure of 1.1-1.3 T/cm^2, treated in a vacuum at 400-750°C to remove hydrogen and then sintered at 950-1000°C for 1-2 h. Nitridation was carried out starting at 1100°C with a subsequent increase to 1400°C and by sintering at this temperature for 10-20 h.

With a decrease in the content of nitrogen in titanium nitride in the region of its homogeneity the porosity of the sintered articles decreases and, for example, for nitride with 12% N after 4 h of sintering in a vacuum at 2200°C is a total of 4%, after hot pressing in argon at 2100°C – 5% [232].

Zirconium nitrides. The phase diagram of the zirconium – nitrogen system in the investigated region of compositions, plotted by Domagala, Pherson and Hansen [198], is shown in Fig. 64.

Zirconium iodide was used as source material. To produce alloys zirconium was nitrided at a temperature of 800-1200°C for 4-12 h. The samples obtained were remelted in an electric arc furnace with a permanent [nonconsumable] electrode. Homogenization was carried out at 1200°C for 48 h with subsequent tempering for hardening.

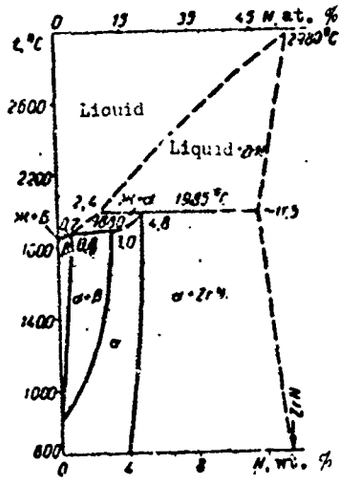


Fig. 64. Zirconium – nitrogen phase diagram.

The β-solid solution forms on cooling according to a peritectic reaction: the liquid phase is 0.7 wt. % (4.4 at. %) N + α-phase is 3.0 wt. % (16.8 at. %) N → β-phase is 0.8 wt. % (5.0 at. %) N at 1800 ± 10°C.

The addition of nitrogen stabilizes the α-variant of zirconium, increasing the temperature of the α → β-transformation. The α-solid solution forms at 1985 ± 15°C according to a peritectic reaction:

The liquid phase is 2.4 wt. % (13.5 at. %) N + ZrN → α-phase is 4.8 wt. % (25 at. %) N.

The maximum solubility of nitrogen in β-Zr is 0.8 wt. % (5.0 at. %) at the temperature of the peritectic reaction and descends to zero at the temperature of the α → β-transformation, equal to 862°C.

The solubility of nitrogen in α-Zr is at the temperature of the formation of the α-solid solution 4.8 wt. % and it drops with a decrease in temperature, reaching 4 wt. % at 600°C.

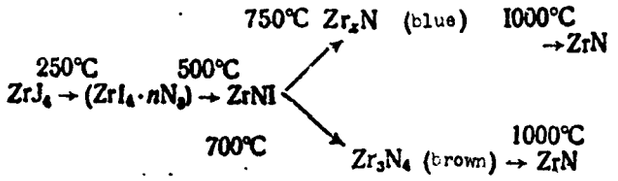
The lower boundary of the region of homogeneity of ZrN lies at 11.5 wt. % (~46 at. %) N at a temperature of 1985°C. It is necessary to note that in work [198] it was not possible to produce zirconium nitride of stoichiometric composition (13.3 wt. % N) and it was not possible to investigate the region of homogeneity of this compound. The melting point of ZrN was taken as equal to 2980 ± 50°C.

The data on the study of the Zr-N system [198] agrees well with the earlier results of other works; thus, an increase in the temperature of the α → β-transformation with the addition of nitrogen was noted in works [199, 200]; the solubility of nitrogen in α-Zr, equal to about 20 at. %, also coincides well with the data of work [198].

Thus, in the system only one stable connection was detected — the nitride ZrN, although earlier there were reports about the existence of one more nitride with 13 at. % N [201].

However, as was noted in [248, 249], the action of ammonia on the zirconium tetrahalides produced nitride phases, containing more nitrogen than in the nitride ZrN. Accordingly [248], the effect of ammonia on Zr at ~750°C, and also on $ZrCl_4$ and $ZrBr_4$ at higher temperatures produced the nitride Zr_xN of dark-blue color with

$0.940 > x > 0.812$. The determination of the density (6.1-7.4 g/cm^3), the change in the parameter of the crystal lattice, the electrical conductivity (about $3 \cdot 10^{-2}$ $\Omega^{-1} \cdot cm^{-1}$) and the magnetic properties (the preparations are diamagnetic) makes it possible to assume that the nitride contains tetravalent of zirconium ions, and also trivalent nitrogen (Zr_3N_4). This nitride crystallizes to a defect lattice of the NaCl type with vacant sites in the zirconium sublattice and a lattice parameter, varying within the indicated limits of the compositions from 4.556 to 4.440 Å. In work [249] in an analogous way according to the scheme



zirconium nitride of brown color, and a composition, corresponding to the formula Zr_3N_4 (a density of 5.9 g/cm^3, a magnetic susceptibility at room temperature of $\chi_g = 0.03 \cdot 10^{-6}$) was produced. Both nitrides at a temperature of 1000°C lose their nitrogen excess are converted onto the stable mononitride ZrN.

The causes of the formation of nitrides of such composition can be the following. The formation of the nitride Zr_3N_4 is due to the ionic bond between the zirconium and nitrogen atoms, arising upon the transfer by the zirconium atom of all its valence electrons ($4d^2 5s^2$) to the nitrogen atoms, which in this case should acquire an s^2p^6-configuration. However for nitrogen (the electron configuration of an isolated atom is s^2p^3) both the formation of an s^2p^6-configuration due to the acquisition of the electrons of its partner by combining, and also the transfer of one electron to its partner with the formation of a stable sp^3-configuration are possible. As a rule, for nitrogen atoms the second possibility is realized (for example, in the nitrides BN, TiN, ZrN), and the realization of the first possibility, i.e., of the complete attraction of the valence

electrons of its partner, becomes probable for hereditary reasons (in this case – the tetravalence of the zirconium in the halide, the formation by nitrogen of a s^2p^6-configuration in ammonia). Thus, in a number of compounds ZrN...Zr_3N_4 the statistical weight of s^2p^6-configurations of zirconium atoms is increased. This transition from the set of d^0- and d^5-configurations for the zirconium atoms and the sp^3-configurations of the nitrogen atoms with a considerable fractions of nonlocalized electrons to the high statistical weight of d^0- and s^2p^6-configurations with intense localization of the electrons in these configurations is due to the variation in the character of the conductivity from metallic for ZrN to semiconductor for Zr_3N_4, and also to the reduction in paramagnetism to its complete disappearance for Zr_3N_4.

In work [998] the structure of one of the preparations with an excess of nitrogen (a deficiency of zirconium) was investigated. The composition of the preparation was $(Zr, 2\%\ Hf)_{0.95 \pm 0.03}, N_{1.0}$, its density was 6.884 ± 0.003 g/cm^3 (the density of stoichiometric ZrN according to these data was 7.284 g/cm^3). The cell maintain 3.913 moles with 3.5% vacant cation sites (8 per cell) and 1.1% vacant anion sites. The nitrogen excess is 0.19 atoms per cell.

The width of the region of homogeneity of the ZrN phase, according to [202], is from 40 to 50 at. % (9.5-13.3 wt. % N). With an increase in the nitrogen content in the region of homogeneity of the ZrN phase, according to [202], the absolute value of thermo-emf increase is, the Hall coefficients and the specific electrical resistance decrease and hardness increases (Table 59).

The electrical resistance here varies nonlinearly, which is characteristic for nitrides with larger fractions of ionic bonding (see Fig. 5), and considerably steeper than for titanium nitride which indicates a high rate of accretion in ZrN of the ionic bonding fraction with the decrease in its nitrogen content. The Hall effect near the lower boundary of the region of homogeneity of zirconium nitride is positive which indicates mainly P-type conductivity of alloys of this composition.

Table 59. The variation in the physical properties of zirconium nitride in the region of homogeneity.

Conditional formula	N content		Thermo-emf, $\mu\Omega$/deg (with respect to copper)	Specific electrical resistance, $\mu\Omega \times$ x cm	Hall coefficient $R \cdot 10^6$, cm^3/A	Microhardness, kg/mm^2
	wt. %	at. %				
$ZrN_{0.675}$	9,41	40,3	—0,98	190	+5,5	—
$ZrN_{0.76}$	10,5	43,3	—4,0	75	+1,2	—
$ZrN_{0.818}$	11,1	45,0	—5,4	58	—1,4	850±42
$ZrN_{0.87}$	11,93	46,8	—7,7	37	—1,45	1060±53
$ZrN_{0.93}$	12,52	48,2	—7,5	30	—1,4	1260±76
$ZrN_{0.956}$	12,83	48,9	—7,4	28,5	—1,3	1390±110
$ZrN_{0.99}$	13,2	49,8	—7,3	28	—1,3	1520±85

It is necessary to note that, according to [978], the electrical resistance of zirconium nitride in the region from 45 to 50 at. % nitrogen varies linearly and attains at 45 at. % greater values than is shown in Table 59 (∿200 μΩ·cm as compared to 58 μΩ·cm). There is also a certain difference in the course of the variation of the thermo-emf in the region of homogeneity. According to [978], the thermo-emf is very small and is practically constant within the limits of 35-40 at. %, and then increases strictly linearly up to 50 at. % of nitrogen attaining for this a saturated composition of the order of 8 μΩ/deg, which is close to the data of Table 59.

According to [978], within the limits of the region of homogeneity the magnetic susceptibility of zirconium nitride varies strictly linearly from ∿40 (at 35 at. % N) up to $22 \cdot 10^{-6}$ (at 50 at. % N).

In Fig. 65 the temperature-concentration dependence of the electrical resistance of zirconium nitride on nitrogen content within the limits of its region homogeneity is shown. It is evident that for alloys with a nitrogen content, close to 50 at. %, the dependence of electrical resistance on temperature is practically linear and is typical for metallic conductivity. With a decrease in nitrogen content the variation in electrical resistance then passes through a maximum at temperatures, decreased with a reduction in the nitrogen content. Then the resistance decreases, as for

semiconductors which indicates the widening of the energy gap between the sd-states of zirconium and the sp-states of nitrogen, corresponding to the increase in the ionic bond fraction. The more rapid increase in the ionic bond fraction with the decrease in the nitrogen content in zirconium nitride in comparison with titanium nitride is very apparent in Fig. 4, on which by dotted lines the nature of the variation in the microhardness of the compositions, typical for metallic state is shown.

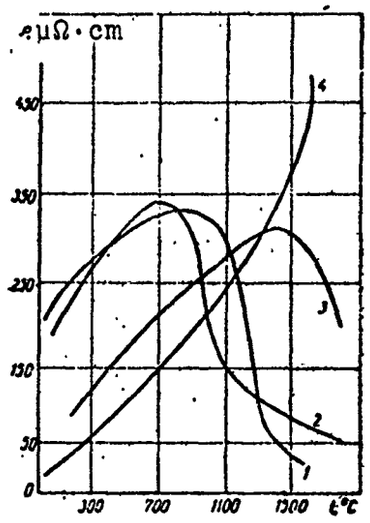


Fig. 65. The temperature-concentration dependence of the electrical resistance of ZrN in the region of homogeneity. 1 – 40.3 at. % N; 2 – 34.3 at. % N; 3 – 48.8 at. % N; 4 – 49.4 at. % N.

The results of a study of the effect of the chemisorption of nitrogen on the Hall effect and the electrical resistance of thin films of metallic zirconium [250] showed that the electrical resistance increases which is connected with the decrease in the effect thickness of the metallic layer. Actually the effect is caused by the transfer of a portion of the electrons by the nitrogen atoms (in the rearrangement of configuration s^2p^3 to sp^3) to the nonlocalized state – in the overall association with the nonlocalized electrons of zirconium and by the increase with this of the fraction of electrical resistance, caused by the interaction between the nonlocalized electrons.

In work [252] the thermoemission properties of zirconium nitride on samples, prepared by the reaction sintering of briquets of zirconium powder in a nitrogen medium at a temperature of 1300°C during the cause of 4 h were investigated. The work function is ϕ = 3.78 eV.

The radiation factor of the nitride according to these data increases within the temperature limits of 800-2000°C from 0.73 to 0.76 (when λ = 655 nm).

The coefficient of cathode sputtering of zirconium nitride upon bombardment by argon ions with an energy of 50-200 eV is equal to 0.026 mole/ion which is substantially less than the cathode sputtering of metals (for example, for tungsten the coefficient of cathode sputtering is equal to 0.23 at./ion).

Zirconium nitride ZrN of saturated composition is a yellow-brown-colored powder with a golden tinge; in the compact state it has a lemon-yellow color with a metallic luster.

In contrast to titanium nitride, which decomposes upon being heated in a vacuum into titanium vapor and nitrogen, zirconium nitride vaporizes with decomposition into solid zirconium and nitrogen [203]

$$ZrN_{тв} \rightarrow Zr_{тв} + {}^1/_2 N_2.$$

The equilibrium constant $K_p = p_{N_2}^{1/2}$ is equal to, according to [203]:

$$\lg K_p = -\frac{17408}{T} + 1{,}48 \cdot 10^{-4} T + 4{,}467,$$

the nitrogen pressure depending on the temperature is determined by the expression

$$\lg p_{N_2} = -\frac{34816}{T} + 2{,}96 \cdot 10^{-4} T + 8{,}934.$$

Table 60 gives data on the vaporization rate and the vapor pressure of zirconium and nitrogen depending on temperature.

Table 60. The vaporization rate of zirconium nitride and the nitrogen of the nitride.

Temperature, °C	Vaporization rate $G \cdot 10^6$, g/cm²·s	Pressure of nitrogen, $p_{N_2} \cdot 10^6$, at.
2236	0,534	0,915
2259	1,299	2,397
2318	1,979	5,583
2333	2,714	4,477
2344	3,020	5,536
2151	14,981	28,96
2466	16,127	31,04

The heat of formation of ZrN determined from these data is $\Delta H^0_{298} = 72.53 \pm 0.43$ kcal/mole, which is close to the data, obtained earlier in work [117], according to which:

t, °K	298,16	500	1000	1500	2000
$-\Delta H$, kcal/mole	82,2	82,1	81,7	81,6	80,9

The $H^0_{298.15}$ for ZrN is equal to 87.3 ± 0.4 and $F^0_{298.15} = -80.5$ kcal/mole [213].

In contrast to the data of [203], in work [210], where the equilibrium in the zirconium-nitrogen system at high temperatures was investigated, it was established that at temperatures of from 2200 to 2800°K and at pressures of from 0.1 to 300 mm Hg of zirconium nitride (in its region of homogeneity) dissociates with the liberation of nitrogen and with the formation of not of metallic zirconium, but of phases poorer in nitrogen as compared to the initial ones

$$ZrN_x = ZrN_{x-\Delta} + \frac{\Delta}{2} N_2.$$

In Fig. 66 the variation of x in the formula ZrN_x is shown depending upon temperature at different pressures. The authors of work [210] accept the possibility of the presence of a noticeable vapor pressure of the zirconium of ZrN_x only at temperatures of 2600-2800°K.

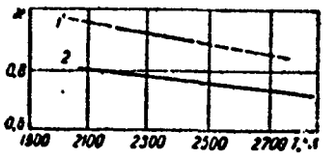


Fig. 66. The dependence of the composition of zirconium on the nitridation temperature; 1 — ∿10-100; 2 — ∿0.1 mm Hg.

The dependence of the heat capacity of ZrN on temperature is represented by the expression [206]

$$C_p = 11{,}10 + 1{,}68 \cdot 10^{-3} T - 1{,}72 \cdot 10^{-5} T^{-2} \text{ [cal/deg·mole]}.$$

In work [207] the heat and free energy of formation of zirconium nitride in the region of homogeneity were determined. It was demonstrated that with an increase of the nitrogen content in zirconium nitride both these values increase (Table 61). It is noted that the effect of the variation in the heats of formation and the decrease in free energy is substantially greater (by ∿2 times) than for carbide systems. This is explained by the sharp variation in the character of the chemical bond with the variation in the nitrogen content within the limits of the region of homogeneity.

Table 61. Variation of the heats of formation and the free energy in the region of homogeneity of zirconium [207].

Formula of the nitride	Heat of formation, kcal/mole	Variation in entropy $\Delta S°_{298}$	Free energy of formation ΔF_{298} for oxygen-free nitrides
$ZrN_{0,56}\ O_{0,02}$	57,5±0,7	—12,7	—52,3
$ZrN_{0,69}\ O_{0,00}$	68,7±1,8	—15,4	—64,1
$ZrN_{0,74}\ O_{0,00}$	72,2±0,9	—16,5	—67,3
$ZrN_{0,89}\ O_{0,03}$	84,5±0,5	—20,4	—76,3
$ZrN_1\ O_{0,04}$	90,7±0,2	—22,9	—81,1

The diffusion of nitrogen into solid and powdered zirconium has been studied in many works. In work [208] the kinetics of the nitridation of zirconium were investigated in the temperature interval 862-1043°C at nitrogen pressures of from 10 to 300 mm Hg; from the obtained data the activation energy was calculated, which was equal to 52 kcal/mole. In work [209] the diffusion of nitrogen into β-Zr at temperatures of 920-1640°C and a pressure of 1 at. was studied. Nitrided zirconium contains 97.8-98.2% Zr, 1.8-2.2% Hf and traces of O, N, H, Fe, Si. The nitridation constant is described by the expression

$$K = 5{,}0 \cdot 10^3 \cdot \exp(48000/RT)\ [(\text{ml}/\text{cm}^2)^2\text{s}],$$

the temperature dependence of the coefficient of diffusion

$$D = 1{,}5 \cdot 10^{-2} \exp(-30700/RT)\ [\text{cm}^2/\text{s}].$$

The solubility of nitrogen in β-Zr increases linearly with temperature and at 1600°C attains 0.6 wt. %. In the interval 920-1640°C solubility can be determined by the equation [199, 204].

$$C = -2810\,T^{-1} + 1{,}42\ [\text{wt. \%}].$$

According to Gulbransen and Andrew [179], the activation energy of nitridation of α-Zr is 39.2 kcal/mole (Figs. 67, 68).

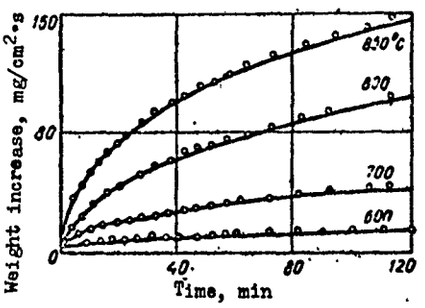


Fig. 67. Kinetic curves of the nitridation of zirconium.

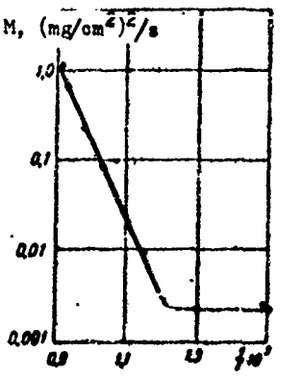


Fig. 68. The temperature dependence of the reaction rate constant Zr + 1/2 N_2 (E = = 39.2 kcal/mole).

The results of an investigation of the kinetics of the nitridation of zirconium powder [178] showed that the diffusion of nitrogen into α-Zr with the formation of a solid solution occurs with an activation energy of 20.0 kcal/mole (at 500-600°C), into α-Zr with the formation of zirconium nitride - with an activation energy of 5 kcal/mole (at 600-1000°C) and into β-Zr — with an activation energy of 2.8 kcal/mole. The low values of activation energy are connected with the use of very thin zirconium powder, whereas in the above-indicated works solid zirconium or shavings or coarse powders was used.

The authors [222] investigated the nitridation at 700-1200°C of solid magnesiumthermal zirconium, melted in a crucible. It has been shown that zirconium nitride, forming on the surface of the metal at a temperature of up to 1000°C, does not penetrate deep into the metal, but yields a thin film on its surface. Upon prolonged heating (up to 24 h) at higher temperatures (1100-1200°C) the nitridation depth reaches about 1.5 mm. It was demonstrated by X-ray diffraction analysis that the nitride with a cubic lattice forms only in a thin surface layer, under it is located a layer of solid solution in α-Zr and below it a base of β-solid solution.

With an increase in the dispersibility of the zirconium powder being nitrided the time of nitridation and the apparent activation energies, entering into the equation of the nitriding reaction constant, are sharply reduced. This reduction with an increase in the degree dispersibility is intensified due to the high heat of

formation of zirconium nitride that also leads to a decrease in the apparent activation energy. The latter effect is expressed to an even greater degree the higher is the ratio of weight of the formed nitride to the weight of the particles being nitrided, increasing with the increase in dispersibility. It is also necessary to keep this in mind in cases of the formation of nitrides of other metals, having high values of heat content.

The addition of 5% KHF_2 to the zirconium catalytically accelerates the nitridation process [246].

In work [253] an investigation of the diffusion of nitrogen in zirconium by the method of internal friction was carried out, however definite conclusions concerning the mechanism of the elementary act of diffusion were not obtained.

The thermal conductivity of zirconium was investigated at temperatures up to 1100°C [211]. The thermal conductivity of zirconium nitride is somewhat less than titanium nitride, and varies more moderately with temperature than TiN (Fig. 69).

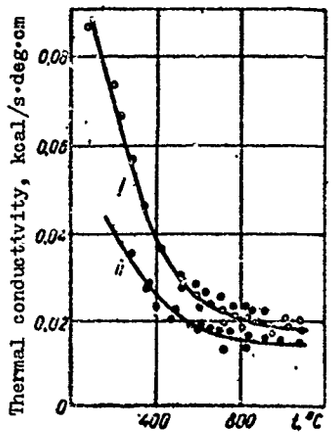


Fig. 69. The temperature dependence of the thermal conductivity of TiN (I) and ZrN (II).

The thermal expansion of zirconium nitride was studied in rather great detail Beydler [212] on the nitride, obtained by the heating of zirconium for 4 h at a temperature of 1250°C in nitrogen and containing 52.7% Zr, 47.2% N and 0.05% Mg. The lattice parameter of a at 17,445 and 680°C was equal respectively to 4.5745, 4.5861 and 4.5965 Å. The coefficient of thermal expansion α is in the interval 17-445°C $(6.0 \pm 0.5)\cdot 10^{-6}$, and in the interval 17-680°C $\alpha = (7.0 \pm \pm 0.5)\cdot 10^{-6}$.

The ZrN is a superconductor [140, 219] with a critical temperature increasing from 3°K for $ZrN_{0.932}$ to 9.5°K for $ZrN_{0.984}$ [1069]. The thermoemission characteristics of ZrN are not of technical interest [170, 221]; the saturation current at 2000°K is a total of 0.05 A (see also p. 75).

According to [1031], the elastic modulus of nonporous zirconium nitride is equal to 51,000 ± 1500 kg/mm^2, (the characteristic temperature is 580 ± 10°K). According to [1077], E = 40,000 kg/mm^2, Θ = 645°K.

Chemical properties. Nitride of zirconium in powdery state in the cold is rather resistant to the effect of many mineral acids, especially hydrochloric, nitric, perchloric, and also mixtures of the acids with oxidizers [214]. Upon heating the solubility in acids and their mixtures sharply increases; after 2-3 h zirconium nitride is completely dissolved in concentrated H_2SO_4, mixture of HNO_3 + HF, H_2SO_4 + K_2SO_4. In alkaline solutions (with a concentration of up to 10%) zirconium nitride does not dissolve even with heating; in more concentrated alkalis and mixtures of alkalis with oxidizers of the perhydrol type dissolution occurs insignificantly. Atmospheric oxygen does not oxidize zirconium nitride up to 900-1000°C. The ZrN is one of the stablest in this respect of the nitrides (it is somewhat inferior to titanium nitride) [9].

Refractory properties. In work [215] an investigation was conducted on the character of the interaction of zirconium nitride with refractory metals upon heating to high temperatures in vacuum. Zirconium nitride is stable under these conditions, considerably more stable than titanium nitride. Up to 2100°C ZrN does not interact for 5 h with tantalum, tungsten; with molybdenum a weak reaction begins with heating at 2100°C for 5 h; with niobium it reacts considerably already at 2000°C; below this temperature in contact with niobium zirconium is completely stable.

Methods of producing zirconium nitride. The basic method of preparing zirconium nitride is the direct nitridation of zirconium powder [178]. The optimum temperature of the nitridation of zirconium powder with nitrogen is 1200°C. The process of saturating zirconium with nitrogen in dissociated ammonia occurs more slowly: a temperature of not less than 1400°C is necessary. Hydrogenated zirconium will form the nitride upon reaction with nitrogen at high temperatures of the order of 1300-1400°C. The method of the direct nitridation of zirconium with the formation of the nitride was used in work [213], where rather coarse zirconium shavings (0.002-0.003 inches) were nitridation for 5 h at 1300-1400°C. In work [203] upon nitriding of zirconium hydride ZrH_2 in a stream of nitrogen at 1050°C for 21 h a product was obtained, whose composition is described by the formula $ZrN_{0.973}$.

An original method of producing technical zirconium by nitriding metallic zirconium was proposed in work [216]. It consists of the nitridation of moist zirconium powder using for heating the powder to temperatures, necessary for active nitridation, the heat of oxidation of zirconium and the heat of formation of zirconium nitride. According to these data, upon heating moist zirconium powder in a stream of nitrogen at 450-600°C for 15 min products are obtained, containing 9.5-10.2% nitrogen, i.e., hydroxy-nitrides of zirconium or technical nitride, which in a number of cases can be used instead of pure ZrN.

Another method of producing zirconium nitride, first used in the work of Friederich and Sittig [110], consists in the reduction of zirconium dioxide with carbon in a nitrogen medium

$$ZrO_2 + 2C + {}^1/_2N_2 \rightarrow ZrN + 2CO$$

at temperatures up to 1300°C. The obtained product contains, besides zirconium nitride (to which they first ascribed the correct formula ZrN), 7-10% impurities, insoluble in sulfuric acid and consisting of ZrO_2 and other impurities. The reproduction of this method showed the impossibility of producing pure zirconium nitride. Obviously, this is connected with the fact that zirconium nitride, according to thermodynamic calculations, is stable in a mixture with carbon up to 1000°C, and with an increase in temperature the reaction

$$ZrN + C \rightleftarrows ZrC + {}^1/_2N_2$$

should shift to the right with the formation of the more carbon-enriched solid solution ZrC-ZrN. The temperature dependence of the equilibrium constant of the interaction reaction of zirconium nitride with carbon is expressed by the equation

$$\lg K_p = -\frac{5290}{T} + 2{,}76.$$

which quantitatively expresses the low stability of the nitride in contact with carbon at increased temperatures [232, 1079].

Zirconium nitride is obtained by the method of accumulation from the gaseous phase on a tungsten or zirconium filament from a mixture of $ZrCl_4$ and NH_3 or $N_2 + H_2$ at a temperature of the filament of 2000-2400°C, and from a mixture of $ZrCl_4 + N_2$ – at 3000°C [45, 159, 184, 217, 218].

The authors [251] developed a method of producing zirconium nitride by reduction of zirconium dioxide with magnesium in the presence of nitrogen

$$ZrO_2 + 2Mg + {}^1/_2N_2 = ZrN + 2MgO.$$

This reaction has a formal significance, since the reduction of ZrO_2 with magnesium under thermodynamic conditions should proceed not to the metal, but to a solid solution of oxygen in zirconium (9.3 at. % oxygen at 1000°C), which is further reduced by the nitrogen due to the additional liberation of free energy as a result of the formation of zirconium nitride.

Technologically upon the reduction of ZrO_2 with magnesium in a nitrogen medium at a temperature of 1100°C of zirconium nitride, containing 13.3% nitrogen, possessing a cubic face-centered lattice with the parameter a = 4.575 Å, i.e., the obtained nitride is close in composition to ZrN. A deficiency of this method if the necessity of washing magnesium oxide from the reduction product which lengthens and complicates the technological process.

In recent years continuous methods of producing ZrN have been developed and rather widely used [1047]. A diagram of a device for the continuous production of zirconium nitride is shown in Fig. 70. Zirconium powder is loaded into hopper 1 by the vibration transmitted to the hopper by the vibrator 2; it spills through grating 3 and in the atomized state due to its own weight falls downward; it enters into the reactor heating zone, where it enters in reaction with nitrogen. The produced zirconium nitride is accumulated in receptacle 5, placed in chamber 6. The reactor heating is carried out with the help of electric furnace 7. The temperature in the reactor is 1200°C; the flow rate of the zirconium powder is 0.5 kg/h; the nitride yield is 0.55 kg/h; the expenditure of electric power is 16 kWh/kg of nitride.

Hafnium nitrides. A phase diagram of the hafnium-nitrogen system has not been plotted; it is only known that hafnium will form one nitride HfN with nitrogen, which was first produced and identified by Van Arkel [217] and Moers [184]. This compound has a metallic character with a very high melting point and a cubic structure.

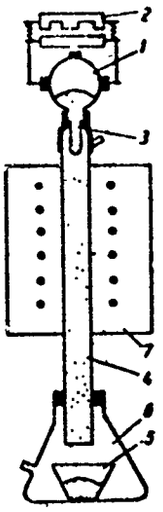


Fig. 70. Diagram of a device for the continuous production of zirconium nitride.

The nitridation of metallic hafnium at temperatures of 876-1034°C and at pressures of 38-402 mm Hg was investigated in work [223]. The nitridation was carried out on sheet hafnium (with a thickness of 0.2 mm), thoroughly purified after rolling and annealed in a vacuum of 10^{-4} mm Hg at 970°C for 1 h. It has been demonstrated that the kinetics of the nitridation correspond to the simple parabolic law of saturation rate

$$W^2 = K_p t + C,$$

where W is the weight of the nitrogen per unit of surface area of the sheet hafnium, t is the nitridation time, K_p is the reaction rate constant, C is a constant, representing the error at the initial moment of observation. The activation energy of the nitridation reaction of hafnium calculated from the obtained data was equal to 57 $\pm$ 3 kcal/mole. The X-ray diffraction analysis of the stable golden-yellow films, forming on the surface of the samples with nitridation, shows the presence along the metal lines also a line of cubic hafnium nitride. Hafnium nitride is obtained by the nitridation of hafnium for 1 h at a temperature of 1400°C and at a nitrogen pressure, equal 1 at. The lattice parameter of this product was 4.50 Å (calculated density is 14.0 g/cm^3). From a compairson of the activation energies and the reaction rate constants of the nitridation of tianium, zirconium and hafnium it is apparent that hafnium possesses maximum activation energy and the lowest nitridation rate (Table 62).

Table 62. A comparison of the activation energies and reactions rates of the nitridation of titanium, zirconium and hafnium [223]

Metal	Activation energy, kcal/mole	Reaction rate constant, $(g/cm^2)^2/min$	Temperature, °C	Literature
α-Ti	36	$1,9 \cdot 10^{-9}$	550—850	[179]
α-Zr	39	$7,8 \cdot 10^{-10}$	400—825	[179]
β-Zr	52	$3,8 \cdot 10^{-10}$	862—1043	[208]
α-Hf	57	$1,8 \cdot 10^{-10}$	876—1034	[223]

In work [224] hafnium nitride was produced by nitriding at 1400-1500°C for 10 h fine shavings of hafnium, containing 2.4% Zr, and also Fe, C, Ti, Cr, W, Ni, Zn, Al, Si, Cu impurities and traces of Mn, Mo, Pb, Mg, Sn. The obtained nitride samples were used for thermochemical investigations. The values of the heat of formation $\Delta H^0_{298.16} = -88.24 \pm 0.34$ kcal/mole and the decrease in free energy with the formation of hafnium nitride $\Delta F^0_{298.16} = -81.4 \pm 0.5$ kcal/mole were found. The entropy of hafnium nitride, determined in this same work was $S^0_{298.16} = 13.1$ cal/deg·mole.

The authors [252] assume that the work function of hafnium nitride during thermionic emission should be at 1700°K 3.85-3.90 eV.

In works [232, 255] the interaction between hafnium nitride and carbon according to the following reaction was investigated

$$HfN + C \rightleftarrows HfC + {}^1/_2 N_2.$$

It was demonstrated that the limiting link in the process of achieving equilibrium is diffusion in the solid phase. The temperature dependence of the equilibrium constant in the interval 1700--2300°C is described by the equation

$$\lg K_p = -\frac{3380}{T} + 2{,}00,$$

from which it follows that at low temperatures the nitride is stabler, and at high temperatures – carbide of hafnium. Even at 1200-1300°C about 50% of the hafnium nitride goes into solid solution with hafnium carbide.

The nitridation of hafnium powder with nitrogen was investigated in work [225]. It was determined that hafnium nitride of stoichiometric composition will be formed at 1200°C in the course of 1 h of nitridation. The temperature dependence of the rate constant of nitridation changes at 700-800 and 1000-1100°C.

$K_{500-700^\circ C} = 1{,}51 \cdot 10^{-4} \exp(-910/T)$ (the formation of a solid solution in α-Hf)

$K_{800-1000^\circ C} = 2{,}75 \cdot 10^{-4} \exp(-2940/T)$ (the formation of HfN)

$K_{1100-1400^\circ C} = 2{,}75 \cdot 10^{-4} \exp(-4000/T)$ (the formation of HfN).

According to the Van Arkel method [217], hafnium nitride is produced by precipitation from the gaseous phase, consisting of a mixture of hafnium chloride, hydrogen and nitrogen bromide on a tungsten filament, heated to 1100-2700°C [159]. The possibility of producing hafnium nitride is indicated by the reduction of hafnium oxide with carbon in a stream of nitrogen [159].

Hafnium nitride is a yellow-brown powder with an olive tinge; it possesses metallic conductivity with a very low specific electrical resistance. Hafnium nitride is more heat-conductive than the nitrides of titanium and zirconium; it possesses the least (of

these nitrides) thermal expansion, and also moderate hardness. The melting point, according to ruff [29], is equal 3310°C, and according to more exact data [254] – to about 3000°C.

The chemical stability of hafnium nitride has hardly been studied; it is assumed that it should be very high [9].

As is reported in [1034], upon the dissolution of hafnium nitride in 6% HF the liberation of hydrogen occurs as a result of the occurrence of these reactions

$$HfN + 3HF = HfF_3 + NH_3,$$
$$NH_3 + Hf = NH_4F,$$
$$HfF_3 + Hf = HfF_4 + {}^1/_2H_2.$$

Thus, hafnium in hafnium nitride has a valence of 3+, and nitrogen a valence of 3-, in other words, the nitrogen atoms form due to the addition of three electrons of the hafnium atoms of an s^2p^6-configuration, and the hafnium atoms – mainly d^0 and d^5-configurations that determines a certain fraction of ionic bonding in hafnium nitride along with metallic and covalence bonding.

For stoichiometric nitride with a lattice constant of a = = 4.5118 Å and a density of 13,386 g/cm^3 calculated from this the pycnometric density was established, equal to 11,696 g/cm^3 which indicates the presence of defectiveness in both sublattices of the nitride. This defectiveness can be estimated at 12.63%. It is necessary to note that the data were obtained not for pure hafnium nitride, but for hafnium nitride, containing 4.5% of zirconium nitride.

3. Transition-Metal Nitrides of Group V

Vanadium nitrides. The vanadium – nitrogen system has been little studied and it only is possible to consider the established existence in it of two nitride phases – V_3N and VN [256]. The system was most completely investigated by Hahn [257] on the basis of the data of X-ray diffraction analysis. Nitrogen is only insignificantly soluble in vanadium. The alloys, containing up to 9.3% nitrogen ($VN_{0.37}$), are two-phase (α-solid solution and the β-phase).

The β-phase of V_3N is homogeneous in region from $VN_{0.37}$ to $VN_{0.43}$ (V_3N-V_2N), i.e., from 9.3 to 10.5% nitrogen in the vanadium. With an increase in the nitrogen content the lattice constants of the hexagonal β-phase increase (Fig. 71). In the region from 10.5 to 16.4% N the alloys are two-phase (β- and γ-phase), from 16.4 to 21.5% N ($VN_{0.71}$-$VN_{1.00}$) the region of homogeneity of the γ-phase spreads, corresponding to the formula VN. The lattice constant of this cubic phase also varies sharply with an increase in the nitrogen content (Fig. 71).

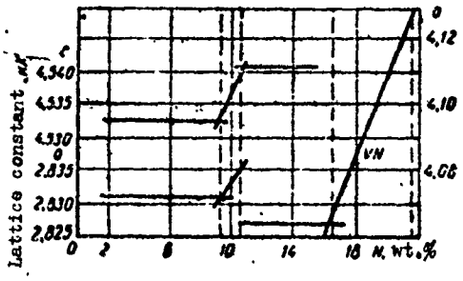


Fig. 71. The dependence of the lattice constants of the phases in the V-N system on the nitrogen content.

Vanadium nitride VN_x has subtraction structure, where in the interval 600-1200°C part of the points of vanadium is vacant, and above 1200°C – a part of the points of nitrogen. At low temperatures hydroxy nitrides $V_xN_yO_{x-y}$ can be formed. The nitrogen atoms are replaced by oxygen atoms, i.e., a substitution structure is imposed on the subtraction structure. The lattice constant (Tables 63, 64) has its maximum at a ratio of $V_{1.0}{\cdot}N_{1.0}$, and the maximum value of the grinding ability is due to the same composition. The lattice constant of VN, determined precisely, is 4,12$_9$kX [259].

Table 63. The atomic composition of oxygen-containing vanadium nitride at various temperatures.

Temperature °C	Formula composition
600	$V_{0.9}N_{0.94}O_{0.06}$
800	$V_{0.94}N_{0.94}O_{0.06}$
1000	$V_{1.0}N_{0.98}O_{0.02}$
1200	$V_{1.03}N_{0.96}O_{0.04}$
1300	$V_{1.14}N_{0.98}O_{0.02}$

Table 64. The dependence of the composition and the properties of oxygen-containing vanadium nitride on the reaction temperature $V_2O_3+2H_2+N_2=2VN+2H_2O$.

Temperature °C	Time, h	Chemical composition, % V	N	O	Formula*	Lattice constant a, kX	Density g/cm³	Specific electrical resistance μΩ·cm	Grinding ability, arbitrary units
600	16	76,6	21,8	1,0	$VN_{0.96}$	4,113	5,12	5,8	0,020
800	2	77,2	21,28	1,52	$VN_{0.98}$	4,126	5,4	3,8	0,033
1000	2	78,4	21,1	0,5	$VN_{1.016}$	4,13	5,83	3,2	0,064
1200	2	78,9	20,8	0,3	$VN_{1.14}$	4,128	5,86	6,6	0,066
1400	2	80,1	18,9	0,5	$VN_{1.17}$	4,12	5,78	5,6	0,056

*Disregarding the oxygen content.

As can be seen from Table 65, according to [257], the difference in the pycnometric and X-ray diffraction values of density is small which attests to the limited number of vacant points in the lattice, in any case, it is much smaller than in titanium nitride [257].

Physical properties. Powdered vanadium nitride is grayish-brown in color with a violet tinge; the preparations with a saturated nitrogen content – bronze color. Vanadium nitride is thermodynamically rather stable; the decrease in free energy upon its formation from metal and nitrogen is expressed by the equation $\Delta F = -60000 - 1{,}73T\lg T + 26{,}38T$ (±10% in interval 298-2000°K).

Table 65. The dependence of the specific gravity of vanadium from the nitrogen content.

Composition	Specific gravity	
	pycnometric	calculated
$VN_{1,00}$	6,040	6,102
$VN_{0,87}$	5,988	6,089
$VN_{0,72}$	5,972	6,066
$VN_{0,38}$	5,967	5,967

The heat content varies according to the equation [260]

$$H_T - H_{298,16} = 10,94T + 1,05 \cdot 10^{-3}T^2 + 2,21 \cdot 10^5 T^{-1} - 4096 \text{ kcal/mole},$$

and the heat capacity

$$C_p = 10,94 + 2,10 \cdot 10^{-3}T - 2,21 \cdot 10^5 T^{-2} \text{ [kcal/deg·mole] (from 400 to 1611 K).}$$

The entropy of VN is equal, according to [261], to 8.91 ± ± 0.04 kcal/deg·mole.

An X-ray spectral investigation of the K-absorption spectra of vanadium in the nitride VN compared with the hydrides, carbides, and borides of this metal, and also with vanadium pentoxide showed that the fine structure of the basic K-absorption edge of vanadium in the pentoxide, carbide and nitride are qualitatively close [267]. However with respect to the variation in the relative intensity of the long-wave white absorption line in the transition from the oxide to the nitride it is possible to draw conclusion about the change in the covalence of the bond.

It is necessary to consider that with the formation of the nitride phases of vanadium a certain increase in the statistical weight of the d^5-configurations of the vanadium atoms occurs, having in the isolated state $3d^34s^2$-configuration both due to the attraction of a portion of the s-electrons of vanadium to the d-shell, and also due to the nitrogen electrons, liberated during the transformation of the s^2p^3- to the sp^3 configuration. The formation of high statistical weights of rather highly isolated (in an energy regard) d^5- and sp^3-configurations causes certain peculiarities in the physical properties of the vanadium nitrides, in particular the melting of VN at 2050°C with decomposition. Also connected with this is the ability of VN to be converted to superconductive state at a comparatively high temperature (7.5°K) [275]. A remarkable property of the nitride VN is its very low thermal coefficient of electrical resistance, being from 100 to 1200°C a total of 0.01%/deg. The basic physical properties of the vanadium nitrides are given in Table 66.

The oxygen impurity in vanadium nitride (about 3% O) causes the anomalous behavior of the temperature dependence of electrical resistance: to 450°C the resistance of this nitride noticeably increases with temperature, then drops, then increases again [955].

Chemical properties. Vanadium nitride VN is insoluble in hydrochloric and sulfuric acids; it is decomposed when boiled in nitric acid, when heated with sodium hydroxide and boiled in a solution of potassium hydroxide [110]. At room temperature the aqueous solutions of alkalis practically do not decompose vanadium nitride VN [276]. With prolonged boiling in concentrated sulfuric acid it is slowly decomposed with the liberation of ammonia. When heated in air vanadium nitride VN is rather stable, being oxidized only at 500-800°C. Vanadium nitride V_3N is much less stable in a chemical regard than VN.

Table 66. Properties of Vanadium Nitrides.

Characteristic	β-V_2N	γ-VN
Region of homogeneity	$VN_{0,37}$—$VN_{0,48}$	$VN_{0,7}$—$VN_{1,00}$
Nitrogen content, wt. %	9,22—10,6	16,3—21,5
Crystal structure	Hexagonal	Cubic
Lattice constant, Å:		
a	2,835 [257]	4,12₉ [259]
c	4,541	
c/a	1,60	
Density, g/cm³	5,967 [257]	6,102 [257]
Melting point, °C	—	Decomposes at 2050°C
Heat capacity (at 298°K, kcal/mole·deg)	—	11,57 [260]
Heat of formation, kcal/mole	—	60,0±2,0 [47]
Energy (298°K), cal/deg	—	21,0±0,1 [261]
Specific electrical resistance, Ω/cm	123—10 [289] ($VN_{0,336}$)	85,4 [289] ($VN_{0,93}$)
Thermal coefficient to electrical resistance, %/deg	—	0,01*
Coefficient thermo-emf, μV/deg	—5,3±0,2 [289] ($VN_{0,138}$)	—4,6±0,8 [289] ($VN_{0,93}$)
Hall coefficient x10⁴, cm³/C	—0,9±0,1 [289] ($VN_{0,336}$)	—0,45±0,16 [289] ($VN_{0,93}$)
Thermal conductivity, cal/cm·s·deg	—	0,0270±0,007 [289] ($VN_{0,93}$)
Transition to the superconductive state, °K	—	7,50—8,20 [304, 275, 100]
Microhardness, kg/mm²	1900±102 [289] ($VN_{0,336}$)	1520±115 [289] ($VN_{0,74}$)
Radiation factor (λ = 655 μm) at 800-2000°C	—	0,77 [252]
Work function upon thermoemission (1700°K), eV	—	3 252

*Determined by S. N. L'vov and V. F. Nemchenko.

Obtaining methods. The action of nitrogen on vanadium powder can produce vanadium nitride of the exact composition VN [257, 177]. For preparing alloys with lower nitrogen content Hahn [257] pressed briquets of mixtures VN and vanadium powder with their subsequent heating in a closed quartz tube at a temperature of 1000-1100°C for 24 h. Upon heating a vanadium wire in nitrogen vanadium nitride powder of bronze color will be formed [237]. In preparing vanadium nitride by the simultaneous reduction of the oxide with carbon and nitridation V_2O_3 is usually used, since V_2O_5 is very volatile.

However, even with this the nitride is difficult to produce, since at 1200°C the nitride in the presence of carbon is converted into carbide. The rather pure nitride was first produced in this manner by Friederich and Sittig [110]. They heated a mixture of V_2O_3 + 3C in a molybdenum boat in a tubular furnace with a porcelain tube at 1200°C in a nitrogen medium (the nitride contained 21.1% N instead of the 21.55%, expected for VN). By heating the vanadium in a stream of nitrogen at 1200°C, they obtained a nitride, containing 21.69% N.

Vanadium nitride was also prepared by heating $VOCl_3$ or V_2O_3 in a stream of ammonia [256].

Epel'baum and Ormont [258] produced vanadium nitride by decomposing ammonium vanadate in a stream of ammonia at 1000-1100°C (at higher temperatures mixtures of VN with vanadium oxides will be formed). Later this method was successfully employed by Hahn [257] to prepare very pure vanadium nitride. Epel'baum and Ormont [258] produced vanadium nitride by the simultaneous reduction and nitridation of the lower oxide of vanadium V_2O_2 at 500-600°C according to the reaction

$$V_2O_2 + 2H_2 + N_2 = 2VN + 2H_2O + 16 \text{ kcal}.$$

A systematic investigation of the conditions of forming vanadium nitride by nitriding metallic vanadium powder was made in work [178]. Nitridation was carried out at 500-1500°C. The saturation of metallic vanadium with nitrogen at 500-800°C obeys the linear law; at higher temperatures – the parabolic law with certain deviations in the initial period. An increase in the temperature much more strongly affects the increase in the nitrogen content than an increase in the exposure time. At temperatures of the order of 1400-1500°C a saturated nitrogen content is reached after 10-15 min. The saturation of vanadium with nitrogen in an ammonia medium occurs more slowly than in a nitrogen medium. From the data of X-ray analysis it follows that at 800-900°C the V_3N phase will be formed, and with an increase in the nitridation temperature – the VN phase. The

parameter of the crystal lattice of vanadium with an increase in the nitrogen content from 0 to 3.5% increases from 3.03 to 3.09 Å. The V_3N phase is detected by X-ray diffraction analysis at a nitrogen content of 2.5-3.0%; this phase lasts up to a nitrogen content of 11.3%. After 12.8 wt. % of N a phase is detected with a lattice parameter of a = 4.13-4.14 Å. The rate of the nitridation reaction decreases from $1.7 \cdot 10^{-5}$ at 500°C to $3.71 \cdot 10^{-4}$ g/cm^3 at 1200°C. The activation energy of the nitridation of vanadium powder is small and is in the region of 500-800°C (the formation of V_3N) about 4640, and in the region 900-1200°C (the formation of VN) – about 4400 cal/mole.

The activation energy upon the diffusion in the compact vanadium above, for example, in a solid solution of nitrogen in vanadium it is 36-37 kcal/mole [305]. The optimum conditions for producing the V_3N phase consist in the heating of the powder at 900°C for 1 h, and VN – at 1200-1300°C for 4 h.

It is possible to prepare vanadium nitride by the precipitation method on a tungsten wire from mixtures of VCl_4 with the equimolar gas $N_2 + H_2$. The optimum conditions are: a temperature of 1540-1570°C, an overall pressure of 50-60 mm Hg, the vapor pressure of the VCl_4 is 8 mm Hg, the diameter of the tungsten wire is 0.20 mm. The obtained product is close in composition to VN [301].

The pure vanadium nitride VN will be formed upon the decomposition of different salts, containing vanadium and nitrogen. Good results are given by the decomposition at 600°C of the salt $(NH_4)_3VF_6$ or at 800°C – of $(VH_4)_3VO_2F_4$ during the course of 1 h [274].

Articles are prepared from vanadium nitride either by hot pressing of the powder in an argon medium (the optimum conditions: for V_3N are of a sintering temperature of 1850°C, a pressure of 100 kg/cm^2, a time of 3-5 min, a residual porosity of 6%; for VN – a temperature of 1800°C, a residual porosity of 4%), or by the reaction sintering in a nitrogen medium of the intermediate products prepressed from the vanadium powder [232]. In the latter case, although the

specific volumes of the nitride phases of vanadium are 28-29% greater than the specific volume of the metal, the increase in volume is not realized due to a diminution in porosity and the latter is 46-49%.

Niobium nitrides. The niobium-nitrogen system has been repeatedly investigated. According to early data, generalized in [138], there are in the system two chemical compounds – Nb_2N and NbN. A rather complete investigation of the Nb-N system was conducted by Brauer and Jander [277]. The solubility of nitrogen in niobium is less than 4.8 at. %, since even the alloy, corresponding to the formula $NbN_{0.05}$, contains a niobium nitride phase. The α-solid solution has a cubic body-centered lattice with a parameter, very slightly differing from the lattice parameter of pure niobium (3.2948 kX). The β-phase Nb_2N is homogeneous in the $NbN_{0.40}$-$NbN_{0.50}$ region; it has a hexagonal close-packed lattice with a statistical distribution of the nitrogen atoms in the large pores of the lattice. The lattice parameter a = 3.046 kX in the region of homogeneity does not vary and the value of parameter c with a decrease in the nitrogen content decreases from 4.986 ($NbN_{0.50}$) to 4.947 kX on the boundary with the α-phase ($NbN_{0.40}$). The γ-phase ($NbN_{0.80}$-$NbN_{0.90}$) is isomorphic to the δ-phase in the Ta-N system and has a structure of the NiAs type. The nitrogen atoms are located in the centers of two trigonal prisms from niobium atoms. In the concentration interval $NbN_{0.75}$-$NbN_{0.94}$ there are two phases: $NbN_{0.75}$-$NbN_{0.79}$ with a tetragonal structure of the deformed NaCl type and $NbN_{0.87}$-$NbN_{0.94}$ with an NaCl structure. However a subsequent work by Schonberg [278] demonstrated that the presence of the two phases should be attributed to the presence of oxygen in the samples, i.e., the formation of phases of an Nb-N-O system.

The hexagonal δ-phase (NbN is the π-phase of Brauer), in the saturated case corresponding to the formula $NbN_{0.95}$, has a lattice with an antinickel arsenide configuration of atoms. The nitrogen atoms are located in the centers of octahedrons, built from metal atoms. The ε-phase $NbN_{1.00}$ has a hexagonal lattice; the space group

is D_6^4-P_3^6; MoC (the γ-phase) has an analogous structure and also certain phosphides – TiP, β-ZrP [279]. Brauer and Jander [277] take note of the noncorrespondence between the cited data about the phases of the Nb-N systems and the data of Umanskiy [280], who for the sample $NbN_{0.65}$ obtained a hexagonal lattice, the parameters and atomic arrangement of which correspond to the δ-phase (NbN is the π-phase of Brauer and Jander). This is possible only under the condition that Umanskiy's nitride contained oxygen, which, being interstitial in the niobium lattice together with the nitrogen atoms, brought the general composition of the phase to $NbN_{0.65}O_{0.3}$. The cause of the noncorrespondence could be incomplete nitridation which was caused by the formation along with the δ-phase of metallic niobium or the α-phase. These expounded results of Brauer were confirmed and definitized in [278, 281, 282, 294].

Researchers [283] proposed a preliminary variant of the phase diagram of the Nb-N system. The system is very complicated; at the present time the existence of a solid solution of nitrogen in niobium and five nitride phases is assumed (Fig. 72). The region of the existence of the solid solution is from Nb to $NbN_{0.025}$. Subsequently there follow the hexagonal β-phase Nb_2N ($NbN_{0.4}$-$NbN_{0.5}$), the tetragonal γ-phase Nb_4N_3 ($NbN_{0.75}$-$NbN_{0.85}$), the hexagonal δ-phase NbN ($NbN_{0.97}$-$NbN_{0.98}$) with an antinickel arsenide configuration, the cubic δ-phase NbN ($NbN_{0.88}$-$NbN_{0.98}$) with a NaCl structure and hexagonal the ε-phase NbN (of saturated composition $NbN_{1.01}$). As follows from the phase diagram (Fig. 72), above 1400°C the α-, β-, γ- and δ-phases are stable and below 1230°C the α-, β-, γ- and ε-phases exist. The diagram of the mutual transformation of the phases in the temperature region from 1200 to 1400°C and the conditions of these transformations are shown in Fig. 73 [281, 282].

In Fig. 74 a phase diagram of the Nb-N system is depicted, plotted from the results of investigation [283]. The existence of the β-, γ-, δ- and ε-phases, found by Brauer were confirmed; the δ'-phase, found by Brauer and Schonberg, was not detected in work [283].

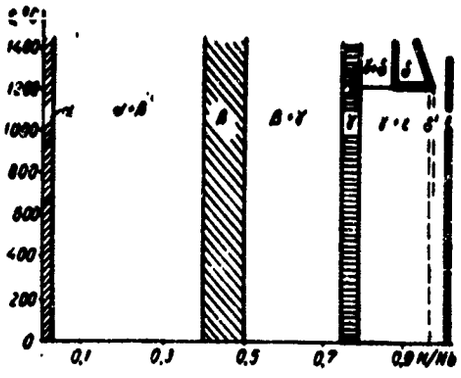


Fig. 72. Phase diagram of the state of the niobium-nitrogen system.

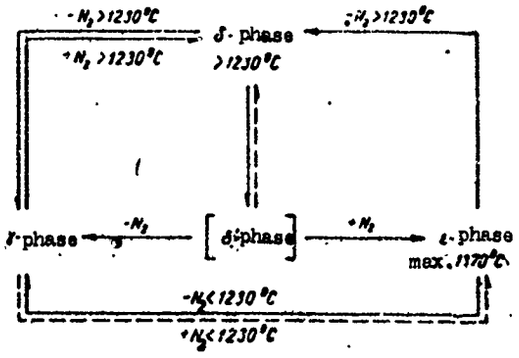


Fig. 73. Transformations of niobium nitride phases.

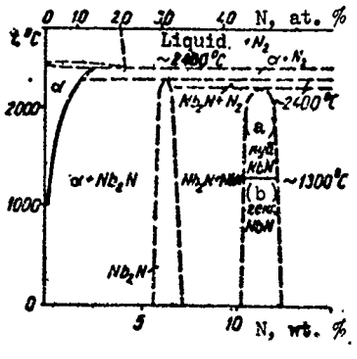


Fig. 74. Phase diagram of the niobium-nitrogen system (according to [283]). KEY: (a) cubic, (b) hexagonal.

The region of the diagram from 0.1 to 30 at. % N in the temperature interval 1600-2200°C was investigated by kinetic methods in work [284].[5] It was demonstrated that under these conditions two well-defined solid phases exist. At low nitrogen concentrations the region of the α-solid solution was detected, the concentration of which varies with temperature and pressure according to the equation

$$C_{N.\alpha} = \sqrt{p} \cdot 7{,}73 \cdot 10^{-4} \cdot \exp(21400/T),$$

where $C_{N.\alpha}$ – is the N connection, in at. %, p is the N pressure, in torr.; T is the temperature, in °K. The solubility of nitrogen in niobium depends on temperature and increases from 3.7 at. % at 1600°C to ∿18 at. % at 2300°C. Within this region the solubility varies according to the dependence

$$C_{N.\alpha}{}_{\text{макс}} = 1{,}48 \cdot 10^{3} \cdot \exp(-11300/T).$$

With a yield beyond the limits of the solid solution the β-phase (Nb_2N) will be formed. Upon rather protracted treatment with nitrogen the α-phase changes to the β-phase with the enthalpy of transition ΔH = -22.6 kcal/g-atom and with the variation in the partial molar standard entropy ΔS^0 = -8.1 kcal/deg·g-atom.

The solubility of nitrogen in niobium in the temperature interval 300-2300°C was also studied in [297]. At a temperature above 1150°C the solubility is C = 720·exp (-20,000/RT), where C is the at. % of N.

As a result of a carefully conducted investigation of the solubility of nitrogen in niobium [1049] somewhat different, as compared to the data of the preceding works, parameters of the dissolution equation were established:

$A \cdot 10^{-4}$	$\Delta\bar{H}_N \cdot 10^{3}$	Literature
6,2	—46,2	[297]
7,73	—42,4	[284]
7,6	—46,2	[1049]

According to [284], the minimum nitrogen content of the β-phase is ∿25 at. %, i.e., less than the ultimate minimum content according to Brauer, equal to about 28 at. %. Between 700 and 2100°C the boundary concentration either does not depend on temperature, or increases somewhat with an increase in temperature. Thus, it is necessary to ascribe to the β-phase a region of homogeneity not of $NbN_{0.4}$-$NbN_{0.5}$, as Brauer did, but a broader one $NbN_{0.33}$-$NbN_{0.5}$.

The existence in the niobium-nitrogen system of α-, β-, γ-, δ- and ε-phases was confirmed in [285] on the basis of the data of X-ray and metallographic investigations. It was demonstrated that the lower boundary of the region of homogeneity of the β-phase lies at ∿26 at. % N, and not at 28 at. % N, as was determined by Brauer. The data of the upper boundary of the region of homogeneity practically coincide with the data of Brauer and Schonberg (50 at. % N). Authors [285] with respect to the variation in electrical conductivity and the Hall effect in the region of the δ-phase at room temperature draw a preliminary conclusion about the incorrectness of Brauer's conclusion concerning the existence of this phase in the stable state only at temperatures above 1230°C.

Brauer and Kirner [295], having definitized the composition of the δ- and ε-phases, showed that the saturated composition of the cubic δ-phase is $NbN_{1.00}$, and the hexagonal ε-phase – $Nb_{0.94}N$.

Comparing the values of the density and the lattice constant, the authors came to the conclusion that the phase with an excess of nitrogen $NbN_{1+\Delta}$ is more correctly examined not as of an interstitial phase of additional nitrogen atoms in the lattice of NbN, but as a subtraction phase of niobium from the lattice of NbN, i.e., a phase of the $Nb_{1-\Delta}N$ type.

Summarizing all the available data, it is possible to consider as sufficiently reliably established in the niobium-nitrogen system the existence of the nitride phases, shown in Table 67.

Table 67. Properties of niobium nitrides.

Characteristic	β-Nb_2N	γ-Nb_2N_x	δ-NbN	ε-NbN
Region of homogeneity	$NbN_{0.38}$—$NbN_{0.50}$	$NbN_{0.75}$—$NbN_{0.85}$	$NbN_{0.58}$—$NbN_{1.00}$	$NbN_{1.00}$—$NbN_{1.06}$
Nitrogen content, wt. %	4,72—7,02	10,1—11,26	11,61—13,1	13,1—13,8
Crystal structure	Hexagonal close-packed	Cubic NiAs type	Cubic NaCl type	Hexagonal γ-MoC type
Temperature range of stable existence, °C	To 2400	To 1500	1230	To ~2300
Lattice constant, A:				
a	3,057—3,050 [283]	—	4,386—4,394 [283]	2,953 [283]
c	4,957—5,005	—	—	11,234—11,257
c/a	1,622—1,641	—	—	3,804—3,813
Density, g/cm³	8,31—8,33 [277]	8,32 [277]	8,30 [277]	7,98 [295]
Microhardness, kg/mm²	1720±100 [289]	1780 [285]	1525±136 [285]	1396±26 [285, 289]
Specific electrical resistance, μΩ·cm	142±6 [285, 289]	90±8 [285]	85±2 [285, 289]	78±4 [285, 289]
Coefficient of thermo-emf, μV·deg	4,6±0,7 [285, 289]	—	1,6±0,1 [285, 289]	−2,24 [285, 289]
Hall coefficient x10⁴, cm³/C	+1,9±0,4 [285, 289]	−0,7±0,1 [285]	+0,5±0,2 [285, 289]	+0,5±0,2 [285, 289]
Thermal conductivity, cal/cm·s·deg	0,0200±0,008 [285,289]	0,0191±0,004 [285]		0,009±0,002 [285],
Heat of formation $\Delta H^\circ_{298,15°K}$, kcal/mole	67,0 [297] 61,1±1,0[303]	—	56,8 [213]	—
Standard entropy, cal/g·deg·mole	22,3[297	—	10,5±02 [47]	—
Heat capacity (298°K), kcal/mole·deg	—	—	10,41 [302]	—
Coefficient of thermal expansion x10⁶, deg⁻¹	3,26[298]	—	10,1 [298]	—
Heat of vaporization, kcal/mole	—	—	91,5 [298]	
Transition temperature to the superconductive state, °K	<1,94[291]	6,8—8,9 [290, 291]	13,1—15,6 [290,291,275]	<1,94 [291]
Radiation factor at 800-2000 °C	—	—	0,83 [252]	—
Work function with thermoemission, (1700°K) eV	—	—	~3,90 [252]	—
Molar magnetic susceptibility x10⁶	—	—	+30 [978]	—
Elastic modulus kg/mm²	—	—	49300±2000	—

Physical properties. The basic physical properties of niobium nitrides were most studied in [285, 289], the results of which are given in Table 67. Below a brief characterization of the structures of the nitride phases of niobium is given; the unit cells of the crystal lattices of these phases are shown in (Fig. 75).

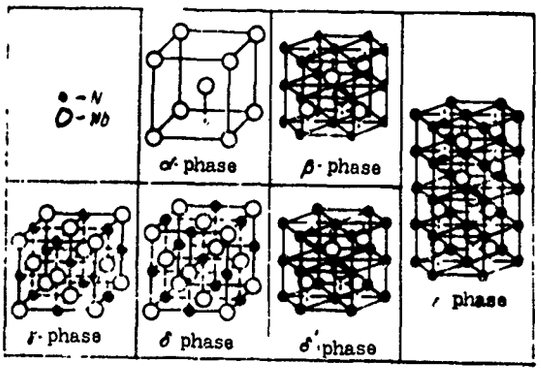


Fig. 75. The crystal structure of nitride phases of niobium.

As the positive values of the Hall coefficient (Fig. 76, [285]) show, the electrical conductivity of a solid solution of nitrogen in niobium and the mixtures of the δ- and δ'-phases, as well as of niobium itself, is mainly of the P-type [hole character]. The P-type [hole character] electrical conductivity of niobium is confirmed by the X-ray spectral investigations of its L_{β_2}-band, which indicates the filling of the larger part of the first Brillouin zone [286]. In the region of the solid solution the predominant effect of the P-type [hole character] electrical conductivity of metallic niobium is preserved. In proportion to the enrichment of the alloys with nitrogen the hole contribution to electrical conductivity decreases and with a content of 27.3 at. % N the electrical conductivity becomes chiefly electronic [P-type] and only for δ + δ'-phase region is hole electrical conductivity [P-type] again observed. The electronic nature [N-type] of the electrical conductivity with relatively high nitrogen contents also agrees with the data of X-ray spectral investigations of the L_{β_2}-band of

niobium in its compounds with nitrogen [286], according to which even with a content of 6.32 wt. % N a considerable decrease in the degree of filling of the first Brillouin zone occurs.

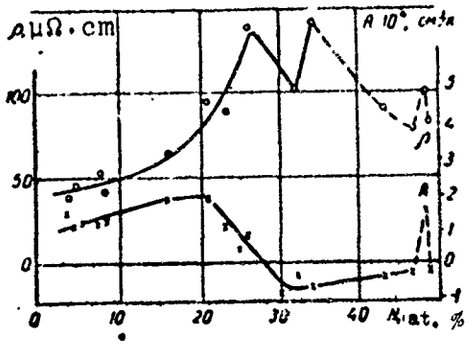


Fig. 76. The concentration dependence of the electrical resistance and the Hall coefficient of alloys of niobium with nitrogen.

The results of X-ray spectral investigation [287] show that for NbN, NbC and NbB_2 according to the decrease in the intensity of the L_{β_2}-and L_γ-bands of niobium with the formation of the indicated compounds it is possible to draw a clear conclusion about the reduction in the density of the d-states in the generalized band. This attests to the fact that with the formation of certain compounds, in particular niobium with nitrogen (NbN), the transfer of the valence electrons of the nonmetallic atoms to the d-band of the metallic atom does not occur, Thus, according to the above-cited data (pp. 9-10), upon the formation of a metallic crystal from isolated atoms of niobium 3.7-3.9 of the valence electrons go over to the localized state (ensuring covalent bonding), and the remaining 1.1-1.3 electrons form an aggregate, then it is possible to assume that with the formation of niobium nitride NbN the transfer of a part of the nonlocalized electrons to the nitrogen atoms occurs with the formation by them of stable s^2p^6-configurations. This process does not have to lead to a noticeable change in the density of the d-states of the niobium atoms as compared to that in a metal. However the statistical weight of the d^5-configurations, formed by the localized part of the valence electrons should be relatively increased, with a simultaneous decrease in the concentration of the free electrons and an increase in the statistical weight of the

nitrogen atoms, having stable s^2p^0-configuration. This causes, in particular, the noncubic symmetry of the ε-phase of niobium nitride NbN (if the nitrogen would give up part of its electrons according to the scheme $s^2p^3 \rightarrow sp^4 \rightarrow sp^3 + p$ to the niobium in the nitride NbN, then the latter would have a cubic structure), and also his high electrical conductivity.

With a decrease in the nitrogen content in niobium nitride NbN (transition from the ε- to δ-phase), apparently, the conditions are created for the transformation of the nitrogen atom according to the indicated scheme with the formation of sp^3-configurations and a mobile electron, capable of partially going over to the niobium atoms, and of partially filling the aggregate of nonlocalized electrons. The latter leads to a certain increase in electrical resistance (see Table 67). Furthermore, the appearance of sp^3-configurations causes the cubic symmetry of δ-NbN and an increase in its hardness as compared to the ε-phase. Subsequently this progresses with the transition to the γ-phase.

The above proposed pattern of the electronic structure of δ-phase niobium mononitride NbN is well confirmed by the data on the thermal conductivity both by its low value, and also by the anomalously high ratio of the calculated electronic thermal conductivity to the measured overall thermal conductivity for this nitride [289].

The same interpretation of it also resulted from an investigation of its superconductivity in the broad interval of nitrogen content in niobium from $NbN_{0.07}$ to $NbN_{1.00}$ [290, 291, 1069]. The hexagonal ε-phase NbN and the β-phase Nb_2N do not manifest superconductivity up to 1.94°K. For the γ-phase Nb_3N_4 the transition point is equal according to these data to 6.8-8.9°K, and the cubic δ-phase changes to superconductivity at 10.62°K (according to other data of these authors – at 13.1°K, and according to now generally accepted data – at 15.6°K). Samples with a small admixture of oxygen give coinciding curves of heating and cooling in the transition region, and samples

without oxygen manifest intense hysteresis. In [292] it was shown that in fields of 0.5-4 Oe and with a stream of up to 20 A an increase in magnetic flux (by 63%) is observed in the transition region of δ-NbN from the normal to the superconductive state (paramagnetic effect), characteristic for pure metals. The transition point of NbN from 11.1 and 12.8% lies within the interval 16.2°K (beginning) and 13.5°K (end) [293].

The superconductivity of the δ-phase of NbN is noted in the behavior of the temperature dependence of the heat capacity [288]. The critical value of the magnetic field, corresponding to the transition to the superconductive state, is equal to 257 G/deg. Thus, superconductivity is possessed only by the cubic δ- and γ-phases, in which a high statistical weight of niobium atoms will be formed with stable d^5-configurations and of nitrogen atoms with stable sp^3-configurations of a localized part of the valence electrons. And there will be formed a peculiar "channel with inert walls" from stable electron configurations, with respect to which without noticeable scattering the current carriers can shift at those temperatures, when these carriers are united in Cooper s^2-pairs and the thermal excitation of the stable configurations, forming "the walls" of the channel is small.

Upon the formation of the β-phase it is possible to assume an increase in the statistical weight of the d^5-configurations of niobium atoms due to the exchange by electrons between them with the liberation here of a part of the electrons of the niobium atoms, which were localized in the metallic crystal, and with their transition partially to the nonlocalized state, and partially to th nitrogen atoms with an increase in the statistical weight of the s^2p^6-configurations of these atoms. A considerable number of current carriers appears which intensifies the electron-electron interaction and leads to the nonsuperconductivity of Nb_2N [275]. For the same reasons this nitride has a relatively high electrical resistance, and also a hexagonal, and not a cubic structure.

In work [284] the thermal stability of phase Nb_2N was investigated under equilibrium conditions and the following expression of the temperature dependence of the transformation of the β-phase → α-phase + N_2 was obtained:

$$p_{\beta \to \alpha} = 5{,}28 \cdot 10^{12} \exp(-66000/T),$$

where p is the nitrogen pressure, in torr.

In work [298] the temperature dependence of the vapor pressure of the nitride NbN was measured by the Langmuir method: $\lg p = 5{,}1 - \frac{20000}{T}$.

Chemical properties. Niobium nitride NbN (apparently, the δ-phase, or produced mixture of the δ- and ε-phases) is very stable in the cold and upon heating in concentrated hydrochloric, perchloric, and sulfuric acids; it is somewhat less stable in dilute hydrochloric, nitric, sulfuric acids, and also in mixtures of acids (in a mixture of nitric and hydrofluoric acids it rapidly and completely decomposes). Hydrogen peroxide and mixtures of alkalis with hydrogen peroxide still more intensively act on it. Aqueous solutions of alkalis upon heating do not decompose niobium nitride intensively; the degree of the action of an alkali on the nitride increases with an increase in the concentration of the alkali in the solution. For analytical purposes concentrated H_2SO_4 and a mixture NaOH with perhydrol are recommended as solvents of niobium nitride.

The Nb_2N is resistant to the action of acids, and upon being heated in solutions of strong alkalis or when fused with them ammonia is not liberated by nitrogen [296].

The oxidation of niobium nitride in air occurs at 500-800°C with the formation of Nb_2O_5.

Production methods. Friederich and Sittig [110] produced the nitride NbN by nitriding a mixture of the oxide (Nb_2O_3) with carbon, where this oxide was prepared by first reducing niobium pentoxide with hydrogen at a temperature of 1100-1200°C. The nitrogen content in the produced nitride was 12.8% (instead of 13.1% as calculated). In work [280] an investigation was made of niobium nitride, prepared by M. M. Babich by heat treating a mixture of niobium with its hydride for three hours in a stream of nitrogen at 1100 and 1300°C.

The basic method of producing the lowest niobium nitrides is by nitriding powdered or compact niobium or by heating mixtures of the highest niobium nitride with niobium.

The kinetics of the nitridation of niobium were studied by Gulbransen and Andrew [179]. They found the dependence of the nitridation rate on time at 400-800°C shown in Fig. 77. The activation energy upon the diffusion of nitrogen in niobium is about 25.4 kcal:mole. In work [284] the solubility of nitrogen in niobium was investigated in detail (see pp. 232-233). It was determined that dissolution obeys Sieverts' law ($\sqrt{p}$). It was calculated that the heat of solution is equal to 21.4 kcal/mole. Similar data were also obtained in [297], where for the equilibrium concentration of nitrogen in solution the following equation was found.

$$C = 1\sqrt{p_{N_2}} \cdot 6{,}2 \cdot 10^{-4} \cdot \exp(-46000/RT).$$

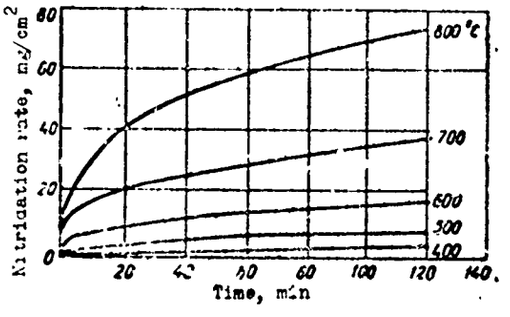


Fig. 77. Kinetic curves of the nitridation of niobium.

Solutions of nitrogen in niobium are close to ideal.

An investigation of the nitridation of niobium powder with nitrogen in the temperature interval of 500-1200°C with exposures of 15-120 min at each temperature [225, 298] showed that up to 500°C after a short period of nitridation (15-30 min) a solid solution of nitrogen in niobium (the α-phase) will be formed, and at temperatures of from 600 to 1200°C – mixture of the nitride phases – β, γ, δ and ε, Upon short exposures (30-60 min) at 900°C the β-phase (Nb_2N) will be formed, and at 1200°C – the ε-phase (NbN) without admixtures of other phases. An analysis of the nitridation curves shows that the saturation of niobium with nitrogen with the formation of the α-phase and the single-phase nitride Nb_2N obeys a law, close to the linear one, and of the NbN phase – the parabolic law. The activation energy upon nitridation of the powder sharply decreases as compared to energy of the nitridation of compact niobium and is from 1/5 to 1/4 of the above-indicated values with the nitridation of compact niobium.

Brauer, Jander [277] and Love [299] prepared niobium nitrides by nitridation niobium powder or shavings in a stream of nitrogen or ammonia. A similar nitridation of niobium shavings for 4-5 h at a temperature of 1300°C makes it possible to produce the highest niobium nitride NbN, and at 1450°C – $NbN_{0.93}$-$NbN_{0.94}$. Nitrides, poorer in nitrogen (from $NbN_{0.88}$ to $NbN_{0.72}$), are produced by the partial elimination of nitrogen upon heating the nitrides NbN in a high vacuum at 1300-1400°C for 3-6 h. Finally, upon heating mixtures of nitrides, rich in nitrogen, with niobium shavings at 1450°C for 3 h in an argon medium alloys, poor in nitrogen (up to $NbN_{0.05}$) will be formed. In an analogous was niobium nitride was prepared by Schonberg [278], who nitridated niobium powder and niobium hydride powder at temperatures of 700-1000°C from 1 h to 2 weeks.

Brauer and Kirner [295] carried out the nitration of niobium powder in a nitrogen medium at 1200-1500°C under pressures of up to 160 at. At temperatures of 1400-1500°C, pressures of from 50 to 150 at. and exposure times of from 2 to 24 h the pure δ-phase will be formed, and at lower temperatures 1200-1300°C and higher pressures 150-160 at. – mixtures of the δ- and ε-phases.

Upon the nitridation of an niobium wire with ammonia for 1 h at 1400-1800°C an external layer of NbN and an internal layer of Nb_2N will be formed on wire [300].

Crystallized nitride deposits are produced by reacting vapors of $NbCl_5$, formed by the vaporization of $NbCl_5$ at 175°C, with a mixture of equimolecular volumes of $N_2 + H_2$ at 1340-1350°C and with an overall gas pressure of 600 mm Hg on the tungsten wire [301].

Researchers [274] prepared the nitride NbN by the pyrolytic decomposition of $(NH_4)_2NbF_7$ in a stream of ammonia at 700°C.

Articles of niobium nitride were produced by sintering of prepressed briquets of Nb_2N and NbN powders at 1900°C in a vacuum with a relatively small nitrogen loss [232]. The produced articles have a porosity of 0.5-1%. Another preparation method is hot pressing at 1800-1850°C at a pressure of 100 kg/cm^2 (the residual porosity is 0.2%; the contamination with carbon is up to 0.3% upon sintering in graphite molds). Articles of niobium nitrides can be produced by reaction sintering of pressed samples of niobium powder in nitrogen at 900-1200°C for 4-8 h, however the porosity of the articles here is not lower than 20%.

Tantalum nitrides. A systematic study of tantalum nitride, discovered in 1876 by Joly, who ascribed to it the formula TaN [138], was only begun in 1924, when Van Arkel produced as a result of a gas-phase reaction a preparation of rather high purity and determined its chemical composition and crystal structure [183]. His work was subjected to critical examination by Hägg [307].

A detailed X-ray diffraction investigation of the Ta-N system was carried out in 1954 by Schonberg [308], and also by Brauer and Zapp [309]. Schonberg demonstrated the presence in the Ta-N system of the following of phases: a solid solution of nitrogen in tantalum with the conditional formula $TaN_{\sim 0.05}$ (β-phase), of the nitrides $TaN_{\sim 0.40}$-$TaN_{\sim 0.45}$ (γ-phase) and $TaN_{\sim 0.80}$-$TaN_{\sim 0.90}$ (δ-phase) and TaN (ε-phase). The cubic lattice of the β-phase differs insignificantly from the cubic body-centered lattice of pure tantalum (α-phase). This superlattice phase has a unit cell constant of a = 3.369 kX (the lattice constant of tantalum is a = 3.311 kX).

It is homogeneous within the limits of $TaN_{\sim 0.40}$-$TaN_{\sim 0.45}$ (γ-phase), is close in composition to the nitride Ta_2N. This classical example of a nitride, formed with respect to a type of interstitial phases with the atomic arrangement of the metal in a close-packed hexagonal lattice and the nitrogen atoms in two octahedral pores, in the centers of the unit cell. The δ-phase, with a region of homogeneity of from $TaN_{\sim 0.80}$ to $TaN_{0.90}$, has a simple hexagonal lattice with an AAA... arrangement of the metallic atoms. The nitrogen atoms are arranged in one of the centers of the two trigonal prisms, formed by the metal atoms.

The hexagonal ε-phase, corresponding to the nitride TaN in the unit cell TaN contains three formula units of the nitride.

Brauer and Zapp [309] detected only two nitride phases Ta_2N and TaN (Table 68). In determining the structure of the TaN results were obtained, completely coinciding with the results of Schonberg (Fig. 78). The shortest distances between the tantalum atoms are 2.90; 2.99; 3.33 kX; the distance of Ta-N is 2.08 or 2.59 kX. The region of homogeneity of this phase is very small, since the alloy $TaN_{0.98}$ already contains the lowest nitride Ta_2N. The latter has a region of homogeneity of from $TaN_{0.41}$ to $TaN_{0.50}$ (instead of $TaN_{0.40}$-$TaN_{0.45}$ according to Schonberg). The tantalum atoms form the simplest hexagonal packing.

Table 68. The properties of the tantalum nitrides.

Characteristic	Ta_2N	TaN
Region of homogeneity	$TaN_{0.41}$—$TaN_{0.50}$	TaN
Nitrogen content, wt. %	3,1—3,86	7,19
Crystal structure	Hexagonal	
Lattice constant, kX:		
a	3,042—3,0415 [309]	5,1808 [309]
c	4,905—4,9088 [309]	2,9049 [309]
c/a	1,62—1,61	0,562
Density, g/cm^3:		
calculated	15,78—15,86 [309]	14,36 [309]
pycnometric	15,42—15,46 [309]	13,80 [309]
Melting point, °C	—	3087±50 [211]
Heat of formation ΔH^0_{298}, kcal/mole	64,7±3 [303] 50,0 [311] (for 24 wt. % N and 1600—2380° C)	60,0±0,6 [213]
	65,2±5 [314]	
Specific electrical resistance ρ (20°C), μΩ·cm	220±15 [318]	180±10 [318]
Hall coefficient $R \times 10^6$, cm^3/C.	—1,4±0,3[318]	—0,6±0,09 [318]
Coefficient of thermo-emf α, μV/deg	—2,17±0,4 [289]	—1,6±0,3 [289]
Work function upon thermoemission (1700°K), eV.	—	4,20 [252]
Thermal conductivity, cal/cm·s·deg	0,0240±0,005 [289]	0,0205±0,009 [289]
Heat capacity (298°K). cal/mole·deg	—	13,10 [47]
Entropy (298°K), deg·mole	—	12,4±1,5 [47]
Temperature of transition in the superconductive state, °K.	9,5 [31]	≤1,20 [304]
Microhardness, kg/mm^2	1220±120 [318]	1080±75 [318]
Radiation factor at 800-2000°C	—	0,79 [252]
Molar magnetic susceptibility $\chi \cdot 10^6$	—	+25 [978]
Elastic modulus, kg/mm^2	—	58700±2000

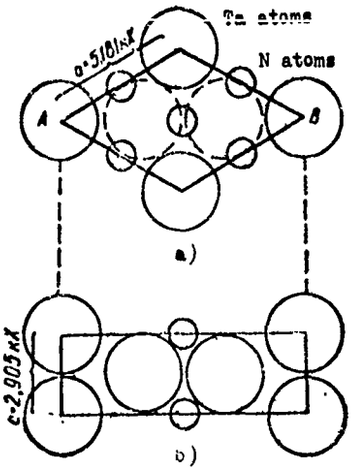


Fig. 78. The crystal structure of TaN (after Brauer and Zapp). a) unit cell. b) its vertical cross section with respect to AB.

According to [312], the region of homogeneity of the Ta_2N at room temperature is from 28 to 33 at. % N which is close to the data of Brauer and Zapp. The δ-phase, ascertained by Schonberg, Brauer and Zapp, was not detected in this work.

However Brauer and Lesser [310] completely confirmed their previous results, and in a survey [256] it was assumed that the $TaN_{0.80}$-$Tan_{0.90}$ phase of Schonberg is an oxygen-containing nitride of tantalum, but not a compound of the tantalum-nitrogen system.

The solubility of nitrogen in tantalum is small. In [311] it was demonstrated that in the temperature interval of 1600-2000°C and at a pressure of 10^{-1} at. tantalum in the solid phase does not dissolve more than 7 at. % N. According to the data of [312], tantalum at room temperature dissolves 2 at. % N, and at 2300°C – 13 at. % N. In the temperature region of 1600-2380°C the connection between equilibrium pressure, nitrogen concentration and temperature is expressed by the relationship

$$C = p^{2.4} \cdot 8 \cdot 10^4 \exp\left(-\frac{43500}{T}\right),$$

where C is the nitrogen concentration, in at. %, p is the pressure, in at.

According to an investigation of the kinetics of nitrogen loss by solid solutions of nitrogen in tantalum in the temperature region 1670-2170°C [984], the heat of solution of nitrogen in tantalum is equal to 82 kcal/mole of N_2. The diffusion of nitrogen in tantalum was studied by the method of internal friction in [313].

Certain data about the interaction of tantalum with nitrogen and air are given in [972].

P. Chiotti [43] showed that TaN at high temperatures, losing nitrogen, is converted to Ta_2N. As was noted in [312], Ta_2N in turn disintegrates with the liberation of nitrogen. This in the temperature interval of 1600-2380°C is described by the equation

$$p = 4{,}5 \cdot 10^8 \cdot \exp\left(-\frac{50000}{T}\right) \text{ [at]}.$$

Thus, it is possible to consider established the formation in the Ta-N of a solid solution of nitrogen in tantalum and the two nitride phases Ta_2N and TaN.

Physical properties. Tantalum nitrides possess a relatively high specific electrical resistance which attests to the energy isolation of the tantalum and nitrogen atoms in the nitride lattices (Table 68). From Fig. 79 it is clear that the acute extremes correspond to the nitride Ta_2N.

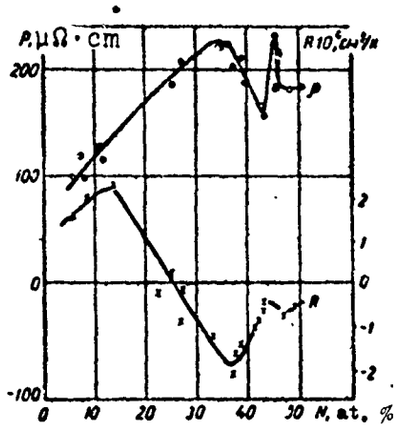


Fig. 79. The concentration dependence of electrical resistance and the Hall coefficient of tantalum alloys with nitrogen.

An electrical conductivity of up to 25 wt. % N bears mainly a hole-type [P-type] character, and at higher contents of nitrogen – an electron-type [N-type] nature concerning which, in particular, the negative sign of the thermo-emf attests. On intense localization of valence electrons near the cores of the tantalum and nitrogen atoms is indicated by the low values of hardness, the high melting point of TaN and the low values of thermo-emf. According to [289], the thermal conductivity of tantalum nitride is of the lattice type, just like semiconductor chromium nitride CrN, i.e., tantalum nitride Tan occupies an intermediate position between the metallic and semiconductor compounds, where, apparently, it is closer to the semiconductors than the metals. Tantalum nitride TaN does not possess superconductivity up to a temperature of 1.20°K; the nitride Ta_2N is a superconductor at 9.5°K.

Of scientific and practical interest are the electrical characteristics of thin films of tantalum nitride of TaN.

The powdered nitride TaN has a color from bluish-gray to dark-gray.

Chemical properties. Tantalum nitride TaN is very stable with respect to most of the mineral acids of any concentrations both cold, and also when heated [276, 315]. It is unstable in dilute H_2SO_4, and also in concentrated when boiling; it is readily dissolved by hydrolysis. It rapidly dissolves in HNO_3 + HF and H_2SO_4 + K_2SO_4. It is unstable in hydrogen [256]. In work [316] data are given on the resistance of tantalum nitride to the action of technical gases. On the whole the chemical properties of tantalum nitrides are close to the chemical properties of tantalum, with the exception of oxidation, which for tantalum begins at 500-600°C, and for tantalum nitrides – only slightly at 800°C.

Production methods. Tantalum nitrides are produced by heating tantalum powder in a stream of nitrogen or ammonia. Horn and Ziegler [317] prepared very pure alloys of tantalum with nitrogen by treating

tantalum powder with nitrogen at a temperature of 1100-1200°C, Schonberg [308] – by nitriding tantalum and tantalum hydride at 700-1100°C from 1 h to 2 weeks. Brauer and Zapp [309] produced nitrogen-rich alloys of the Ta-N system by treating of tantalum powder with nitrogen for 6 h at 1400°C. The kinetics of the process of nitriding tantalum were studied by Gulbransen [179], whose data are given in Fig. 80. The value of the rate constant of reaction varies within the limits of 500-850°C from $9.6 \cdot 10^{-15}$ to $2.84 \cdot 10^{-12}$ $g/cm^3 \cdot s$; the activation energy of nitridation is equal to 39 kcal/mole. The kinetics of nitridation were investigated at higher temperatures in [311, 312].

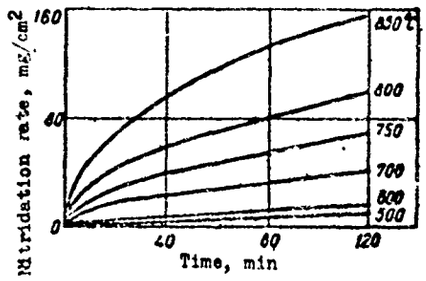


Fig. 80. Kinetic curves of the nitridation of tantalum.

The optimum conditions for producing of tantalum nitrides by treating tantalum powder with nitrogen are: for Ta_2N a temperature of 800-900°C, for TaN – 1200°C with a nitridation time of 1-2 h [178]. To produce the nitride TaN at 1100°C, 5-6 h of the nitridation are necessary.

Chiotti [43] investigated the conditions of preparing tantalum nitride by nitriding the metal with ammonia; at a temperature of 800-900°C and with an exposure of from 5 to 18 h the nitrogen content in the alloy reached a total of 6.12% and on the X-ray photograph only weak lines, belonging to TaN, were detected. The alloy upon being heated in a vacuum at 2000°C lost a part of its nitrogen, being converted into the nitride Ta_2N. With subsequent heating in a vacuum tantalum lines appeared on the X-ray photographs which indicates the subsequent disintegration of the nitride.

Friederich and Sittig [110] prepared tantalum nitride with a content of 6.9% N by heating tantalum hydride in nitrogen.

Upon heating a mixture of Ta_2O_5 and carbon in a stream of N_2 and NH_3 it is not possible to produce the pure nitride; the nitride content in the best case is 10-15%; remainder is the carbide TaC [110]. Analogous products were obtained by treating tantalum powder with nitrogen, containing traces of carbon compounds.

Alloys of tantalum with nitrogen can be produced by precipitating from the gas phase a mixture of $TaCl_5 + N_2 + H_2$, however along with TaN tantalum is liberated, being reduced from Ta_2O_5 by hydrogen. Therefore it is better to carry out the precipitation of the mixture $TaCl_5 + N_2$, but at high temperatures of the order of 2500-2800°C.

The researchers [274] indicate that upon the decomposition at 700-800°C of the compound $(NH_4)_2TaF_7$ preparations will be formed, the composition of which can be expressed by the formula $Ta_3N_5(TaN_{1.67})$, having a reddish-brown color and soluble in boiling concentrated H_2SO_4 and hydrofluoric acid.

The existence of this compound was recently confirmed in [980], where Ta_3N_5 was produced by the action of ammonia on tantalum pentoxide at 800-900°C

$$3Ta_2O_5 + 10NH_3 = 2Ta_3N_5 + 15H_2O.$$

In this work additional characteristics of the properties of the compound were obtained. It was found that it oxidizes in air at 200°C; in a vacuum of 10^{-3} mm Hg at temperatures above 800°C it does not completely lose its nitrogen, being converted into a certain new nitride phase with a black color. With subsequent heating above 1100°C this phase is converted into a mixture of the nitrides TaN and Ta_2N. The density of Ta_3N_5 is equal to 9.85 g/cm^3;

the electrical conductivity of the pressed powder is lower than 10^{-4} $\Omega \cdot cm^{-1}$; it is diamagnetic. Its crystal structure has not yet been sufficiently investigated; according to preliminary data Ta_3N_5 has a tetragonal lattice with constants of a = 10,264; c = 3,893 A.

The formation of a similar nitride will not agree with the data on the tantalum-nitrogen system, however its existence is completely possible since A. Kh. Breger managed to obtain in an analogous way the titanium nitride $TiN_{1.16}$ (see p. 195). This compound, obviously, should possess a high fraction of ionic bonding and the nitrogen atoms should have a high statistical weight of stable s^2p^6-configurations.

To produce ultra athin tantalum nitride powder the action of a stream of hydrogen is used at a temperature of 3000°C on tantalous chloride [1023]. The nitrogen content in this nitride is 6.5% (as compared to the calculated content 7.19% for TaN), with an admixture of oxygen of about 1%; the dimension of the particles is several hundredth parts of a micron.

Articles are prepared from tantalum nitrides by hot pressing of nitrides powders at a temperature of 1800°C and a pressure of 100 kg/cm^3 in an argon medium. The obtained products have a residual porosity of 1.5-2%; the contamination with the carbon of the graphite mole is up to 0.1%. Articles of tantalum nitrides are prepared by the sintering of prepressed intermediate products of nitrides in a vacuum; by the reaction sintering of briquets, pressed from tantalum powder in a stream of nitrogen at 900°C for 8 h for Ta_2N and at 1200°C for 4 h for TaN. The obtained articles have a residual porosity of 9-14%.

4. Transition-Metal Nitrides of Group VI

Chromium nitride. The solubility of nitrogen in solid chromium is slight [321, 334]. In work [323] it was demonstrated that the solubility of nitrogen in chromium is: at 1100°C – 0.04 wt. %; at 1200°C – 0.09 wt. %, at 1300°C – 0.14 wt. % and at 1400°C – 0.26 wt. %.

The data on the solubility of nitrogen in chromium in the temperature interval 700-1320°C, determined in work [943], are close to the data, obtained in [323].

The maximum absorption of nitrogen by liquid chromium is at p_{N_2} = 1 at. about 4 wt. %, [322, 323]. The temperature dependence of the solution constant of nitrogen in chromium in the temperature interval 1600-1750°C has the form [322]:

$$\lg K = \frac{1660}{T} - 0{,}2782. \quad ^{6}$$

The lowering of the general state of the nitrogen in the chomium with an increase in temperature was connected with the exothermic nature of the reversible formation reactions of chromium nitrides from liquid chromium and nitrogen [324]. This was distinctly proven in [322], where it was established that the nitrogen content in the chromium decreases from 4.0842 wt. % at 1600°C to 3.5413 wt. % at 1750°C.

According to [320, 325], in the chromium-nitrogen system two nitrides CrN_x and Cr_2N_x will be formed. The nitride Cr_2N (β-phase) has a region of homogeneity, located according to old data within the limits, of from 11.3 to 11.9 wt. % N, and according to Eriksson [325] - from 9.3 to 11.9 wt. % N. His structure is characterized by the disordered arrangement of the nitrogen atoms in the hexagonal densest packing of the lattice of the chromium atoms, i.e., this is typical interstitial phase of nitrogen in a chromium lattice.

The phase CrN (γ-phase) has a simple cubic lattice of the NaCl type. In works [343, 350] the results of an electron diffraction investigation of the nitride CrN are given.

Physical properties. Chromium nitride in the powdered state is black, and Cr_2N is light-gray in color. The physical properties of these nitrides were investigated in detail in [326-328], where it was noted that CrN is a semiconductor with a forbidden zone width of about 0.24 eV with high electrical resistance, Hall coefficient and thermo-emf (Table 69). The temperature dependence of the thermo-emf and the specific electrical resistance of CrN is shown in Fig. 81. In works [326, 328, 329] the magnetic properties of chromium nitrides were studied, it was established that they are paramagnetic materials with a susceptibility, somewhat greater than pure chromium. In [329] it is noted that the presence of paramagnetism for the chromium nitrides is an indication that they have resonance covalent bonds (after Pauling), since with normal covalent bonds they would be diamagnetic materials or slightly magnetic substances. In work [330] an X-ray spectral investigation was conducted for chromium nitrides in comparison with other compounds of chromium. The presence of a regular variation in the intensity of initial absorption in the series Cr_2O_3, CrN, CrB_2, and also the decrease of the magnetic susceptibility in this series attests to the increase in the fraction of covalent bonding along with the presence of ionic bonding, and also to a decrease in the number of uncompensated spin electrons on the 3d-shell of the chromium atoms. In the compounds Cr_3C_2, CrB, Cr_7C_3, Cr_2N there is observed a greater, than in the above-mentioned series, initial region of K-absorption spectra and a substantially smaller magnetic susceptibility that makes it possible to assume the presence in them of resonance covalent bonding. In hybridization almost all 3d-electron orbits participate with a decrease here in the number of free states and with a considerable increase in number d-states with a p-character. On the whole CrN has ionic-covalent character, and Cr_2N has a covalence-metalltic character [329]. It is also possible to come to the same general conclusion from positions of the concepts concerning the formation by the atoms in the compound

of stable electronic configurations with a minimum of free energy. With the formation of chromium nitride it is possible to assume the acquisition by the chromium atom of a stable d^5s^2-configuration as a result of receiving one electron from a nitrogen atom, having a configuration of localized sp^3-electrons. Such a combination of configurations causes the cubic structure of this nitride, and also the appearance of the energy gap between the states of the chromium and nitrogen atoms with the semiconductor properties following from this. The formation of unpaired electrons on the d-orbit also causes the increased paramagnetism of this nitride. In the nitride Cr_2N it is necessary to consider possible the formation of a high statistical weight of $d^{10}s^2$-configurations of chromium atoms (such configurations in an extreme case should cause antiferromagnetism)[7] with the formation by the nitrogen atoms of a sp^3-configuration and an electron, which is located mainly in the nonlocalized state and causes the metallic properties of this nitride. It is natural, that the paramagnetism of the nitride decreases as compared to CrN and its value approaches, as one would expect the paramagnetism of chromium. The great localization of valence electrons in the stable configurations in CrN causes its great heat of formation as compared to Cr_2N, and the energetic separation of the atoms - its ease of dissociation into elements (at 1500°C). The great localization of valence electrons in CrN is also indicated by the large value of the Hall effect and the low concentration of effective current carriers with their high mobility due to the weak dispersion on the stabilized atomic cores.

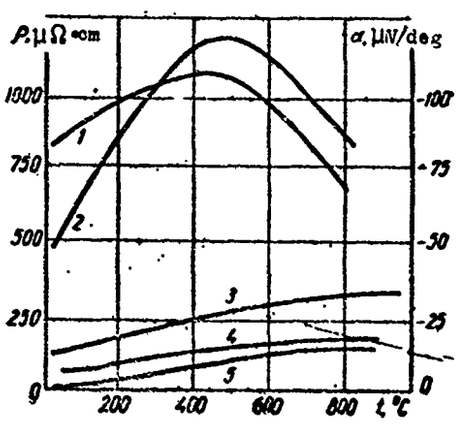


Fig. 81. Temperature dependence of the thermo-emf and the specific electrical resistance of chromium nitrides: 1 - α_{GrN}; 2 - β_{GrN}; 3 - β_{CrN} (15.5% N); 4 - β_{CrN}; 5 - α_{Cr_2N}.

Table 69. Properties of chromium nitrides

Characteristic	Cr_2N	CrN
Nitrogen content, wt. %	11,87	21,7
Region of homogeneity, at. %	32—33,3 [401]	Very narrow
Crystal structure	Hexagonal close-packed	Cubic face-centered
Lattice constants, kX:		
a	4,806—4,760 [401]	4,148 [401]
c	4,479—4,438	—
c/a	0,928	—
Density, g/cm^3:		
calculated	6,51	6,18
pycnometric	—	5,8—6,1 [1]
Melting point, °C	—	At 1500°C it decomposes
Heat of formation $-\Delta H^0_{298}$, kcal/mole	7,6 [322]	23,5 [953]
Temperatures (°C), at which the elasticity upon dissociation is:		
1 mm Hg	—	719 [74]
10^{-3} mm Hg	—	533 [74]
Specific electrical resistance (20 °C), μΩ·cm	79±3 [326, 327]	640±40 [326,327]
Thermal coefficient of electrical resistance, deg^{-1}	+1,78 [326, 327]	3,75 [326, 327]
Thermo-emf μV/deg	−2,2±0,1 [326, 327]	−92±6 [326, 327]
Hall constant (20°C), R x 10^4, cm^3/a	−0,7±0,1 [326, 327]	−260±13 [326, 327]
Effective concentration of current carriers n x 10^{-23}, cm^{-3}	0,89 [326, 327]	0,002 [326,327]
Mobility of the current carriers, u, cm^2/s	0,83 [326, 327]	41,0 [326, 327]
	5,7 [329]	18,0 [329]
Magnetic susceptibility χ x 10^6	5,6 [326, 327]	12,1 [326, 327]
Thermal conductivity, cal/cm·s·deg	0,519 [289]	0,0300** [289]
Microhardness, kg/mm^2	1571±49 [289]	1093±93 [289]
Radiation factor (λ = 655 μm) at a temperature of		
800-1300°C	0,69 [340]	0,60—0,55 [340]
Elastic modulus, kg/mm^2	32000 [1077]	33000 [1077]

*Magnetic susceptibility of chromium, according to [329], is equal to $3,4 \cdot 10^{-6}$

**For $CrN_{0,926}$

Chemical properties. A detailed investigation of the chemical stability of the chromium nitrides was carried out in [276, 315, 341], from which it follows that the nitride CrN is considerably more resistant than Cr_2N to the action of the mineral acids. Aqueous alkaline solutions of both nitrides hardly decompose at all. It is necessary to note [276] that the nitride CrN is along with tantalum nitride TaN one of the stablest of the transition-metal

nitrides, and the nitride Cr_2N is one of the least stable along with the zirconium nitride ZrN. Both chromium nitrides are most completely decomposed by perchloric acid, and Cr_2N, furthermore, – by dilute and concentrated HCl, and also by dilute H_2SO_4 (1:4). The chromium nitride CrN does not react with hydrogen; it burns in oxygen to form Cr_2O_3.

Producing methods. Alloys of chromium with nitrogen are prepared by the nitridation chromium powder with ammonia at a temperature of 800-1400°C [332]. The chromium nitride CrN is also produced by treating with nitrogen at 600-900°C fine pyrophoric chromium powder, prepared by the decomposition of the amalgam [55]. It is also possible to produce the nitrides by the direct sublimation of amalgam in nitrogen.

The authors [953] investigated equilibrium in the chromium-nitrogen system depending upon pressure and temperature by nitriding flaky electrolytic chromium with a purity of 99.40% (the basic impurity is oxygen 0.588%). The temperature was varied within the limits of 1100-1400°C; the nitrogen pressure was 0.5-45 mm Hg. In all cases two-phase samples were obtained, consisting of the chromium nitride Cr_2N and a solid solution of nitrogen in chromium. The measurement of the nitrogen pressure above the two-phase sample of approximately equimolar composition showed that the pressure at 1000°C is 0.5; at 1100°C – 1.5; at 1200°C – 6.6; at 1300°C – 19; at 1400°C – 43.5 mm Hg.

A systematic investigation of the nitridation of chromium powder to produce nitrides was carried out in work [178]. It was demonstrated that the maximum absorption of nitrogen by chromium occurs in the temperature interval 800-1000°C. A temperature of 900-950°C is optimum for producing the CrN phase. In this temperature range the reaction between powdered chromium and nitrogen occurs so actively that it is necessary to increase the supply rate of nitrogen to furnace by 8-10 times. Above 1000°C the CrN phase is unstable and converts to Cr_2N. To produce the single-phase

nitride Cr_2N it is necessary after 2-4 h of exposure at 1200-1300°C to sharply cool (to harden) the obtained product along with the reactor, since with slow cooling considerable aborption of nitrogen occurs with the formation of a mixture of the CrN and Cr_2N phases. The slower the cooling occurs in the temperature interval 1000-800°C, the more CrN will be formed in the obtained product. The reaction between compact chromium and nitrogen was studied in [334] in the temperature range 1000-1300°C. It was determined that the kinetic absorption curves of nitrogen bear a parabolic nature. The activation energy of diffusion was determined to be 23.3 kcal/mole which coincides well with the data of [335] and [336], in which the values of the activation energy of diffusion were found to be respectively 25.7 and 27-28 kcal/mole. The maximum rate of nitrogen absorption is observed at 1100°C; the reaction constant is equal to $2.4 \cdot 10^{-9}$ $(g/cm^2)^2/s$.

Reaction diffusion of nitrogen into chromium begins at a temperature of 700°C; it increases at first slowly, and at 1030°C – very rapidly. This, probably, is connected with the formation above 1030°C of only the Cr_2N phase (below Cr_2N will be formed and on the outside of the samples – CrN); it is also noted that reverse diffusion of chromium does not occur.

Kiessling and Liu [320] prepared chromium nitrides by treating chromium boride with ammonia: at 735°C CrN will be formed, between 800 and 1100°C - a mixture of CrN and Cr_2N and at 1180°C - Cr_2N.

Olson with his colleagues [337] produced a chromium nitride film, by passing ammonia over chromium, degassed in a vacuum (10^{-4} mm Hg). An investigation of the films, produced by a ten-minute nitridation at 950-1000°C, showed that they consist mainly of CrN, at higher temperatures - of a mixture of CrN and Cr_2N and at the highest temperatures - of Cr_2N. These data coincide well with results of work [178, 320]. Chromium in the finely-dispersed state absorbs nitrogen at 800°C [338]; with an increase in a nitrogen pressure absorption is somewhat increased [339].

Methods are known [332] for producing chromium nitrides by heating $CrCl_3$ or CrO_2Cl_2 with ammonia or with magnesium, lithium and other nitrides, however it is doubtful whether all these preparations can be considered pure.

Researchers [274] indicate the possibility of producing chromium nitride CrN by the decomposition of $(NH_4)_3CrF_6$, which begins at 300°C and proceeds to the end at 600°C.

The preparation of articles of chromium nitrides is most effectively carried out by the reaction sintering of intermediate products, pressed from chromium powder in a stream of nitrogen [232]. The optimum temperature for sintering an intermediate product, pressed at a pressure of 1.8 t/cm^2 with the formation of an article of Cr_2N, is 950°C. The obtained articles have a residual porosity of 11%. A reduction in the porosity of a sintered article as compared with a pressed intermediate product occurs as a result of an increase in specific volume with the formation of nitride of chromium; this increase is 40-50%. An analogous method of producing articles from Cr_2N is described in work [234]. It is recommended that the intermediate products of chromium powder be first sintered in argon at 1300-1400°C, for 16 h, then that they be nitrided at 1300°C. However the results obtained were worse; the residual porosity was higher than 30-35%, due to the inactivation of chromium upon prolonged sintering in argon.

Molybdenum nitrides. Molybdenum nitrides were first produced by Urlaub in 1857 and he ascribed to them the formulas Mo_5N_3 and Mo_5N_4 [345]. Rosenhein and Braun [346] produced molybdenum nitride by reacting MoO_3, $MoCl_3$ or $MoCl_5$ with ammonia and gave it the formula Mo_3N_2.

A systematic investigation of molybdenum nitrides by the X-ray analysis method was carried out by Hägg [347], which established in the Mo-N system the presence of three nitride phases: the β-phase Mo_5N_2 ($MoN_{0.40}$), which earlier was ascribed the formula Mo_3N, with

a tetragonal distorted lattice of metallic atoms, a γ-phase Mo_2N with a cubic, face-centered lattice and a δ-phase MoN with a simple hexagonal lattice, analogous the nickel-aresenide lattice. The β-phase is stable at temperatures above 600°C. The region of homogeneity of the Mo_2N phase at high temperatures is displaced in the direction of increased contents of molybdenum (Fig. 82). It follows from this that the products, described by Uriaub, Rosenhein and Braun, were either mixtures of molybdenum nitrides, or defect nitride phases.

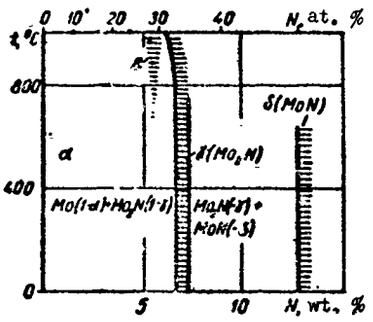


Fig. 82. Phase diagram of the molybdenum-nitrogen system.

Schonberg [348] confirmed Hägg's data who studied in some detail the structure of the δ-phase (MoN).

A subsequent investigation of the structure and compositions of molybdenum nitrides was carried out in the works of Z. G. Pinsker with his colleagues [349-352].

An electron diffraction study of the structure of the γ-phase (Mo_2N), having a cubic lattice, demonstrated that the phase tended toward the formation of subtraction structures with a defect in the molybdenum atoms. Upon investigation the hexagonal nitride δ-MoN it was discovered that actually there are two molybdenum nitrides of this composition with slightly different lattice constants (δ'- and δ"-phase), the δ'-phase is distinguished by a certain displacement of the molybdenum atoms from their particular positions [349, 351]. With a nitrogen deficiency a laminar grain MoN (the δ'-phase) will be formed and with a greater nitrogen content - the δ"-phase. The introduction of a larger quantity of

nitrogen does not increase, but decreases the lattice constant (for the δ'-phase a = 5.72; c = 5.60, for the δ"-phase a = 5.665; c = = 5.520 Å) which is explained by the following circumstances. The lattice of the δ-phase consists of pockets, each of which is formed by three atomic layers (MoNMo), i.e., this lattice is of laminar type. The introduction of additional nitrogen into the prisms between the pockets leads to compacting of the packing, i.e., to "tightening" of the molybdenum atoms. The β-phase is a tetragonal high-temperature modification of the cubic γ-phase with a transition point of 650°C [355].

The solubility of nitrogen in molybdenum is very small; the region of the α-phase is narrow; it is possible to assume that solid molybdenum practically does not dissolve nitrogen [353, 354]. Even with a content in molten molybdenum of 0.0008% nitrogen formation of the Mo_2N phase is observed [356].

The results of an investigation of the adsorption of argon, oxygen, nitrogen and carbon monoxide by powdered molybdenum (with a purity of 99.9%, a specific surface ∿0.5 m^2/g) at -195° and -183°C showed that the adsorption of nitrogen is small and is close to the adsorption of argon (the values of the capacity of the monomolecular layers are close) [357].

Physical properties. The basic physical properties of molybdenum nitrides are given in Table 70. The Mo_2N phase has, apparently, a metallic character [289]. In contrast to the other transition-metal nitrides Mo_2N has a positive sign for the coefficient of thermo-emf which attests to the hole character [P-type] of conductivity. This is also indicated by the positive sign of the Hall constant. The extremely low microhardness of this nitride (630 kg/mm^3) is a result of the severe asymmetry of the distribution of the electron density or the defect structure, which was indicated above. The nitride Mo_2N is thermally unstable and readily converts to the lower nitride Mo_3N.

Table 70. Properties of molybdenum nitrides.

Characteristic	Mo_2N	Mo_2N	MoN
Nitrogen content, wt. %	5,4	6,75	12,73
Region of homogeneity, at. %	Narrow [348]	~32—33 [348]	Narrow [348]
Crystal structure	Face-centered tetragonal	Cubic face-centered	Hexagonal
Lattice constants, kX:			
a	4,160 [347]	4,155—1,160 [347]	5,725 [348]
c	4,016	—	5,608
c/a	0,962	—	0,980
Density, g/cm^3:			
calculated	—	—	9,13 [936]
pycnometric	—	8,04 [347]	8,60 [347]
Melting point, °C	Decomposes	Decomposes at 895°C	Decomposes
Heat capacity (298° K), cal/mole·deg	—	8,98 [360]	—
Heat formation ($-\Delta H^0_{298}$) kcal/mole	—	16,6±0,5 [47]	—
Temperatures (°C) at which the dissociation pressure is:			
1 mm Hg	—	329 [74]	—
10^{-3} mm Hg	—	209	—
Specific electrical resistance $\mu\Omega\cdot$ cm	—	19,8±7 [289]	—
Coefficient thermo-emf μV/deg	—	2,18±0,5 [289]	—
Hall coefficient, cm^3/c	—	2,83±1,2 [289]	—
Thermal conductivity, cal/cm cal/cm·s·deg	—	0,0427±0,007 [289]	—
Microhardness, kg/mm^2	—	630±86 [289]	—
Temperature of the advent of superconductivity, °K	—	5,0 [275, 304]	12,0 [275, 304]

The physical properties of the others phases have practically not been investigated. The nitrides Mo_2N and MoN are superconductors with hith values of transition points [275, 304]. The transition temperature in the superconductive state for Mo_2N is lower than for MoN (5.0 and 12.0°K respectively). It is possible to assume that with the formation of MoN a portion of the nonlocalized electrons of the molybdenum atoms is transferred to the nitrogen atoms with the formation for the latter of an increased statistical weight of stable s^2p^6-configurations which ensures the creation of an "energy channel" from the stable configurations of the molybdenum (d^5) and nitrogen atoms, the slight electron scattering in which leads to the high value of $T_к$. In the case of the nitride Mo_2N it is the same in principle, however the high concentration here of nonlocalized electrons from two molybdenum atoms cannot be substantially decreased due to the capture of electrons by the nitrogen atoms that leads to a decrease in the value of $T_к$. It is also possible that in this case, judging from the cubic symmetry of Mo_2N, the nitrogen atoms will form

sp^3-configurations with the liberation of one electron per atom which also should lead to a reduction in $T_к$ for Mo_2N as compared to MoN.

Chemical properties. When heated in air molybdenum nitrides are oxidized to MoO_3.. There are indications about their spontaneous ignition in air [1].

When heated in argon β-nitride does not vary up to 1000°C; when heated in a vacuum it loses nitrogen; the transition to the α-phase, i.e., practically pure molybdenum [359]. The MoN decomposes in a vacuum more slowly than WN.

Producing methods. Upon the passing of ammonia over molybdenum at a temperature of 850°C only a small fraction of the metal is converted into an alloy by the nitrogen [358]. Hägg [347] prepared molybdenum alloys with nitrogen by passing ammonia over freshly-reduced molybdenum powder at 400-720°C for 4-24 h. Alloys were formed, containing from 0.77 to 7.15% N. Above 725°C these alloys dissociate. To produce a higher nitrogen content of up to 11.95% prolonged nitridation (up to 120 h) at 400°C is necessary. Schonberg [348] prepared molybdenum nitrides by treating molybdenum powder with nitrogen at a temperature of 800°C for several hours. The maximum nitrogen content was 49.6 at. %.

Urlaub [345] produced molybdenum nitrides by passing ammonia over $MoCl_5$ or MoO_3. Molybdenum nitrides were obtained in an analogous way by Rosenhein and Braun [346].

In work [359] the formation of molybdenum nitrides by the simultaneous reduction and nitridation of molybdenum trioxide and ammonium molybdate with a mixture of 70 vol. % N_2 and 30 vol. % H_2 was investigated in detail. As a result in a temperature of 750-800°C the β-nitride is produced. It has been demonstrated that a nitride film forming on molybdenum particles, is semi-impermeable to nitrogen, is hydrogenated with the formation of different compounds of the ammine type which causes the loosening of the film

and ensures the possibility of the continuation of the nitridation process. Upon the nitridation of molybdenum powder with ammonia two nitride phases β and γ will be formed.

According to [178], by treating molybdenum powder with nitrogen the producing of nitrides is hampered. The nitride Mo_2N will be formed by treating powdered molybdenum with ammonia at 700°C for 4 h, where the role of the hydrogen reduces, besides the above-indicated, to the reduction of the molybdenum which activates the subsequent reaction with nitrogen. The molybdenum nitride Mo_2N can also be produced by heat treating of ammonium molybdate in a medium of ammonia at a temperature of 1100°C for 1 h.

Articles of molybdenum nitride Mo_2N are prepared by reaction sintering - by treating of prepressed (at a pressure of 1.8 t/cm^2) intermediate of molybdenum powder with nitrogen at a temperature of 700°C for 8 h [232]. The porosity of the articles produced in this manner is about 20%.

Tungsten nitrides. The tungsten-nitrogen system was first investigated by Hägg [347], which detected the presence of the α-phase - practically pure tungsten, and the β-phase, which has a cubic face-centered lattice and corresponds in composition to the formula W_2N. The insolubility of nitrogen in tungsten was discovered by I. I. Zhukov [338]. The β-phase is analogous to the γ-phase of the Mo-N system. Kiessling and Liu [320] discovered the second variant of the W_2N phase, which will be formed by the nitridation of tungsten at a temperature of 825-875°C and called it not quite fortunately the γ-phase. This phase has a dense, cubic face-centered lattice. Apparently, the γ-phase is identical to β-phase. Schonberg [348] discovered the WN phase (δ-phase) with a content of about 50 at. % nitrogen and having a hexagonal lattice. Kiessling and Liu confirmed the existence of W_2N, however the cubic γ-phase WN was not detected by them. Kiessling and Peterson [361] showed that the γ-phase is in fact hydroxy-nitride, formed by the action on tungsten of ammonia, containing a mixture of oxygen, and

water vapor. The authors also came to the same conclusion [362].

The authors [988] detected the cubic tungsten nitride with the composition W_3N_4 (γ'-W_3N_4) with a lattice constant of a = 4.122 Å; its structure was examined in detail. However it is possible that this phase is a hydroxy-nitride, since oxygen is contained in it (the composition is $W_3[N_{0.95}O_{0.05}]_4$, i.e., the ratio between the nitrogen and oxygen atoms is 19:1).

A subsequent investigation of the phase composition of the W-N system was carried out by the electron diffraction method by Z. G. Pinsker with his colleagues [350, 363-368]. They produced the β-phase (W_2N) in thin films; its cubic face-centered structure was confirmed. According to [347], the lattice constant of this phase is a = 4.118 Å with a content of ∿18.2 at. % which is the lower boundary of the region of homogeneity; the upper boundary corresponds to a stoichiometric composition of W_2N (33.3 at. %). In the lattice of the cubic tungsten nitride (the β-phase) the tungsten atoms do not form a defect face-centered lattice, but the nitrogen atoms are satistically distributed in the center of the cube and on the middle of the cube edges [364, 366]. Subsequent electron diffraction investigations [366-368] established the existence in the W-N system of large series of hexagonal and rhombohedral δ-phases, the scheme of the distribution of which on a phase diagram is shown in Fig. 83. A peculiarity of the structure of the δ-phases (Table 71) is the formation by the tungsten atoms of one-, two- or three-storied pockets, which form a hexagonal or rhombohedral sequence. The nitrogen atoms are disposed either inside the pockets, or between them. The distances between the tungsten atoms are small, and the distances between the tungsten and nitrogen atoms according to the magnitude can be subdivided into two types which indicates the difference in the nature of the forces interacting between the component atoms [366]. A typical element of the structure of one of the δ-phases is shown in Fig. 84. There is a similarity between the structures of the tungsten δ-nitrides and the transition-metal borides both with respect to atomic arrangement, and also in terms

of the magnitude of the interatomic distances. Thus, the nitrogen atoms in the nitride δ_R^V form slightly corrugated layers similar to those, which are observed in borides with structures of the W_2B_5 type. This similarity is of great interest from the point of view of the peculiarities of the electron structure of boron and nitrogen atoms and its variation during the formation of the corresponding phases. For the nitrogen atom the reorganization of the configuration of valence electrons according to the scheme is possible: $s^2p^3 \rightarrow sp^4 \rightarrow sp^3 + p$ with the liberation of one weakly-bound electron. For the boron atom according to energy considerations due to s→p-transition transformation of the configuration of the s^2p-valence electrons occurs into the energetically more stable sp^2-configuration, which, in turn, tends toward still greater energetic stabilization to sp^3 according to schematic diagrams: $2sp^2 \rightarrow sp^3 + 2p$. Thus, the transformations of the configurations of valence electrons in both cases are analogous with only one difference which in the case of boron a large number of readily-mobile electrons will be formed.

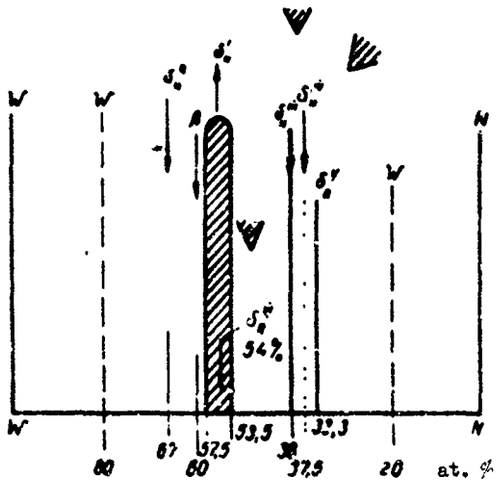


Fig. 83.

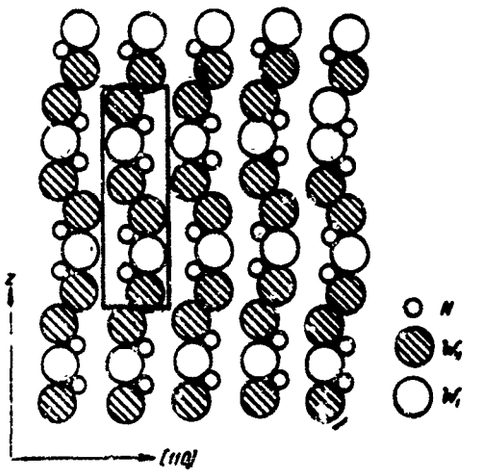


Fig. 84.

Fig. 83. Phase diagram of the tungsten-nitrogen system.

Fig. 84. An element of the structure of the δ-phase of the W-N system.

Table 71. Structural characteristics of the δ-phases of the W-N system.

Phase*	Approximate formula	Space group	Lattice constant Å			Interatomic distances Å		Calculated density g/cm³
			a	c	c/a	W-N	N-N	
δ_H^I	$W_{1,15}$— —$W_{1,35}N$	$P6_3$— —mmc— —D_{6h}^4	2,885	15,30—15,46	5,3—5,35	W_I—N 2,16 W_{II}—N 2,26	2,60—2,62	14,36—15,7
δ_H^{II}	W_2N	$P\bar{3}$—C'_{31}	2,89	22,85	7,9	W_I—N 2,88 W_{II}—N 3,09 W_{III}—N 2,91	2,89	12,0
δ_H^{III}	$W_{0,64}N$	$P6_3/mmc$— —D_{6h}^4	2,87	11,00	3,81	W_I—N 2,14 W—N 2,16	2,75	11,0
δ_H^{IV}	$W_{0,6}N$	$P6_3$—C_6^6	2,89	10,8	3,73	W_I—N 2,16	1,67	10,63
δ_R^V	$W_{0,5}N$	$R\bar{3}m$—D_{3d}^5	2,89	16,1	5,67	W—N 2,915 3,03 3,04	1,71	9,0
δ_R^{VI}	$W_{1,17}N$	$R\bar{3}m$—D_{3d}^5	2,89	23,35	8,07	W_I—N 2,13 W_{II}—N 2,12	3,12	13,6

*H - hexagonal lattice, R - rhombohedral lattice.

Physical and chemical properties. The properties of the tungsten nitrides are given in Table 72. The highest tungsten nitride WN is a brown-colored powder, W_2N is black colored. At 600°C WN decomposes in a vacuum with the formation of the β-phase according to the reaction: $2WN = W_2N + 1.2N_2$. The decomposition of WN occurs much more rapidly than MoN. The tungsten nitrides are resistant to the action of nitric and dilute sulfuric acids and soda sclution [369, 370]. Hot concentrated sulfuric acid decomposes nitrides with the formation of WO_3 and the liberation of ammonia. Aqua regia acts in the same way. Upon fusion with Na_2CO_3 sodium tungstate and ammonia will be formed. With respect to heated in air the nitrides are readily oxidized to WO_3. The nitride W_2N does not manifest superconductivity.

Producing methods. It is very difficult to produce a compound of tungsten with nitrogen by treating tungsten with ammonia, and in the opinion of certain researchers [358, 371] it is not at all

possible. However, Laffite and Grandadarm [372] ascertained that ammonia reacts with tungsten at a temperature of 140°C, but at 200°C the alloy again decomposes to nitrogen and tungsten.

Table. 72. Properties of tungsten nitrides.

Characteristic	W_2N	WN
Nitrogen content, wt. %	3,67	7,09
Color	Black	Brown
Crystal structure	Cubic face-centered	Hexagonal
Lattice content, Å:		
a	4,118 [347]*	2,893 [348]
c	—	2,826
c/a	—	0,977
Density, g/cm³:		
calculated	—	10,52
pycnometric	12,2	12,08—12,12 [348]
Melting point, °C	—	Decomposes at 600 °C
Dissociation pressure in a vacuum, mm Hg		
344°C	1 [74]	—
296°C	10^{-1}	—
256°C	10^{-2}	—
221°C	10^{-3}	—
Heat of formation $-\Delta H^\circ_{298}$, kcal/mole	17,2±3,0 [47]	—
Transition point to superconductivity °K	<1,28 [275, 304]	—
Refractive index	—	5±0,5 [370]**

*For the cubic γ-phrase a = 4,122-4,133 Å.
**It is transparent in thin layers.

At low temperatures (from 20 to 80°C) and comparatively high pressure values (from 10^{-4} to 300 mm) the adsorption of ammonia by tungsten powder prevails, where the adsorptive layer is approximately monomolecular. At high temperatures between 250 and 750°C the formation of an imide occurs first (from 250 to 360°C), and then the nitride W_2N.

The reaction mechanism of tungsten powder with ammonia was studied by Matthias and Frankenberger [374], who determined that at 250-360°C tungsten imide will be formed as an intermediate compound. Hägg [347] by acting ammonia with tungsten at 700-800°C for 48 h managed to produce products with a content of only 1.67% N. However Schonberg [348] reports about preparing tungsten nitrides with a content of up to 41.7 at. % N by treating tungsten powder with dry ammonia for several hours at 800°C.

According to the data, given in Gmelin's reference book, tungsten nitride can be produced by the action of nitrogen on tungsten even at normal pressure, at 550-600°C, but in the presence of catalysts. Without catalysts nitrogen acts weakly on tungsten practically up to 900°C. The nitride will be formed only on the active sites of the surface, covering about 20% of its area with a monomolecular layer. Tungsten nitride, to which in works [332, 373] was ascribed the formula WN_2 with 13.2% nitrogen, will be formed at very high temperatures of the order of 2500°C.

Z. G. Pinsker with his colleagues for an electron diffraction investigation prepared films of tungsten nitrides by nitriding tungsten films (applied by vaporization on a chip of rock salt crystal) with the help of dissociated ammonia with a rather high rate of the latter. With the slow passage of ammonia incomplete nitridation is observed, and also the formation of disordered structures. The nitridation temperature in these works was 700°C and higher [364].

An investigation of the nitridation of tungsten powder was also conducted in [362]. It was shown that nitrides will be formed only by using very fine tungsten powder and by first passing hydrogen to reduce the tungsten with subsequent nitridation in a stream of ammonia. The nitrogen content rapidly increases at temperatures of from 350 to 470°C, attaining the nitride composition WN. At a temperature of 400°C the nitride W_2N will be formed. By treating ammonium tungstate with ammonia the nitride W_2N will be formed at 560°C. The reduction of tungsten anhydride with ammonia leads to the formation of hydroxy-nitride.

Conversely, according to the data obtained in our laboratory, by T. S. Verkhoglyadova, the reduction of WC_3 with ammonia leads to the formation at 300°C of the nitride W_2N, and at 600°C - the nitride WN; 400°C mixtures of these phases will be formed. The treating of tungsten powder with ammonia by heating to 500°C and with an exposure at this temperature of 30-60 min leads to the formation of the W_2N phase and when heated to 1100°C - to formation of a mixture of the W_2N and WN phases.

5. Transition-Metal Nitrides of Group VII

Manganese nitrides. The first works on producing and investigating the manganese nitrides were conducted by Prelinger [385] and [338, 386]. The Mn-N system was first roentgenographically investigated by Hägg [387].

The solubility of nitrogen in α-Mn is a total of 0.156%; the lattice constant with this increases from 8.894 to 8.897 kX. The solubility of nitrogen in β-Mn is somewhat higher; the lattice constant (α) is increased from 6.289 to 6.305 kX. The solubility of nitrogen in liquid manganese at P_{N_2} = 1 at. is expressed by the equation [388]

$$\lg K = \lg C_N(\%) = \frac{3010}{T} - 1{,}457,$$

with a variation here in the free energy ΔF^0 = -13,780 + 6.65 T.

According to Hägg, five nitride phases exist in the system. The δ-phase contains about 2% N; it exists only at high temperatures; between 400 and 600°C breaks up into the α-solid solution and the ε-phase.

The ε-phase at low temperatures (up to 500°C) has, according to Hägg, a narrow region of homogeneity – from 6 to 6.5% N; at high temperatures this region is expanded in the direction of alloys, poor in nitrogen from 3-4 to 6.5% N. The ε-phase can be examined as Mn_4N (5.99% N) with a cubic face-centered lattice of the Mn atoms and an ordered arrangement (it is analogous to the γ'-phase in the Fe – N(Fe_4N) system.

The ε-phase (Mn_2N-Mn_5N_2) has a region of homogeneity of 9.2--11.9%, where the manganese atoms form a hexagonal lattice close packing, and the nitrogen atoms are distributed statistically in the interstices of this lattice. With an increase in the nitrogen content within the region of homogeneity a growth in the lattice constant occurs.

The η-phase (Mn_3N_2), containing a minimum of 13.5% N, and a maximum of 14-15% N, has a tetragonal face-centered lattice. The nitrogen atoms are arranged in it in an ordered manner.

In a subsequent work [389] the temperature regions of the existence of the phases and their region of homogeneity were definitized. It was demonstrated that in the field of the ε-phase it is necessary to distinguish a region of a new phase ε', lying between 9.8 and 15.0 at. % N, and possessing paramagnetic properties With respect to these same data it is necessary to examine the δ-phase as a tetragonal face-centered phase of γ-Mn stabilized by nitrogen, and the ε-phase as a cubic face-centered phase of γ-Mn stabilized by nitrogen. A schematic phase diagram of the manganese-nitrogen system is shown in Fig. 85, plotted by Hägg, with the introduction in it of more precise refinements according to work [389]. Researchers [390] confirmed the existence of the Mn_4N (the ε-phase), Mn_5N_2 (the ξ-phase), Mn_3N_2 (the η-phase) phases. A new phase Mn_6N_5 (the θ-phase) was detected, which is the richest in nitrogen and which crystallizes into a tetragonal face-centered lattice, i.e., the same as Mn_3N_2, differing from the latter by a disorderly atomic arrangement in the lattice. The θ-phase is stable up to a temperature of 580°C inclusively. The arrangement of the phases on a Mn-N diagram can be represented by the diagram of Fig. 85a. Certain data about alloys of the Mn-N system are also given in works [391, 392].

Physical and chemical properties. The properties of manganese have been little investigated; the available data are given in Table 73.

Most completely studied are the magnetic properties of the manganese nitrides [389, 392, 393]. It has been shown that the ε-phase (Mn_4N) is a ferromagnetic material [393], and the ε'-phase is nonferromagnetic. Also established is the paramagnetism of the ξ-phase (Mn_5N_2-Ma_2N). With a variation in the nitrogen content in Mn_4N, i.e., with an increase in the number of defects in the nitrogen sublattice, a decrease in magnetic saturation, magnetic moment and a growth in the Curie point occur (Table 74).

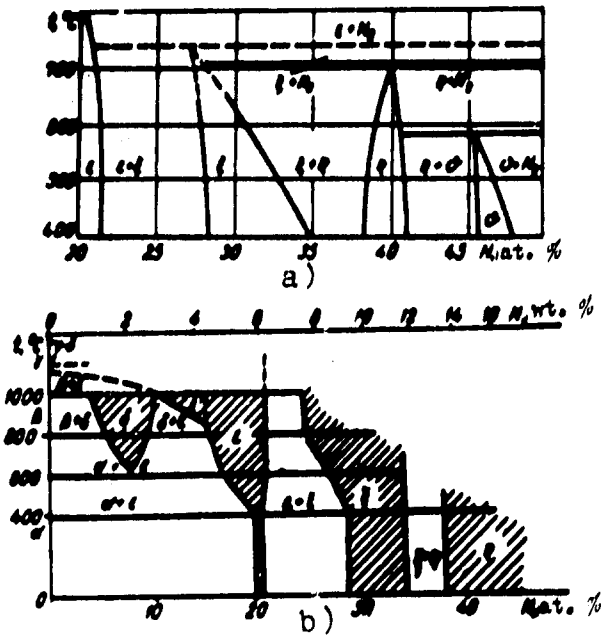


Fig. 85. The manganese-nitrogen system. a) diagram of the phase fields. b) phase diagram.

Table 73. Properties of manganese nitrides.

Characteristic	δ-phase	ε-phase (Mn_4N)	ε'-phase	ζ-phase Mn_5N_2—Mn_2N	η-phase (Mn_3N_2)	θ-phase (Mn_4N_3)
Nitrogen content, at. %						
400°C	—	19,5—20,0 [385]	—	28,4—34,7 [389]	—	45,7—47,9 [390]
600°C	—	16,7—20,7	—	27,5—34,7	—	46,5 (500°C)
800°C	5,3—9,1 [389]	15,6—20,7	—	24,4—?	—	—
						—
1000°C	3,8—9,8	15,0—20,7	9,8—15,0	24,4—?	38,0—44,6 [389]	
Crystal structure	Tetragonal face-centered	Cubic face-centered	Cubic face-centered	Hexagonal close-packed	Tetragonal face-centered	Tetragonal face-centered
Lattice constant, kX:						
a	3,764 [389]	3,860 [389]	3,800 [389]	2,773—2,825 [387]	4,20 [387]	4,214 Å [390]
c	3,729	—	—	4,520—4,528	4,03	4,148 Å
c/a	0,99	—	—	1,630—1,601	0,97	0,984
Density, g/cm³	—	6,76	—	6,2—6,6	6,6	—
Heat of formation $-\Delta H^0_{298,5}$ kcal/mole	—	30,3±0,4 [394]	—	48,2±0,5 [394]	45,8 [112]	—
Entropy, cal/deg mole		—	—	45,9 [47]	35,8 [112]	—
Curie point	—	485—513 [389]	—	475 [389]	—	—
Heat of combustion, kcal/mole	—	411,4—0,2 [394]	—	504,0—0,4 [394]	—	—
Effective magnetic moment, Bohr magnetons	—	1,2 [140]	—	3,94 [140]	—	—

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Table 74. Magnetic properties of the defective (with respect to nitrogen) phase Mn_4N [393].

Nitrogen content, at. %	Value of X in formula Mn_4N_{1-x}* defects)	Lattice constant, kX	Curie point, °C	Magnetic saturation σ,	Magnetic moment, Bohr magnetons
15,23	0,2819	3,810	505	2,45	0,101
16,20	0,2266	3,820	513	6,58	0,272
17,40	0,1568	3,830	510	13,50	0,560
18,61	0,1500	3,834	509	14,26	0,592
19,25	0,0852	3,844	500	19,95	0,828
19,87	0,0099	3,856	494	24,73	1,032
20,00*	0,0000	3,860	483	28,55	1,192

* Extrapolated values

In work [392] it is noted that the magnetic properties of manganese nitrides depend only on the composition, and not on the peculiarities of the production conditions.

Manganese nitrides in a chemical regard are not stable, when heated they readily give off nitrogen. Upon heating the nitrides Mn_2N and Mn_3N_2 with hydrogen ammonia will be formed. Ammonia is also liberated by the interaction of Mn_3N_2 with aqueous solutions of NH_4OH [6].

Production methods. Alloys of manganese with nitrogen are readily produced by the direct nitridation of manganese with nitrogen or ammonia at a temperature of 800-1200°C [332, 338, 386, 390, 392, 395] or by nitriding in a stream of ammonia of the manganese amalgam, formed on a mercury-pool cathode by the electrolysis of $MnCl_2$; with the heating to incandescence of the amalgam in a medium of dry nitrogen the nitride Mn_3N_2 is obtained [6,385].

The authors [390] also prepared manganese nitrides by treating the amalgam Mn_2Hg_5 (which was produced by the electrolysis of manganese on a mercury-pool cathode) with ammonia, nitrogen and mixtures of ammonia and hydrogen. The optimum conditions of this process are given in Table 75.

Table 75. Optimum conditions for production of manganese nitrides by nitriding amalgam.

Phase	Composition of the gaseous medium, vol. %			Temperature, °C	Time, h
	NH_3	N_2	H_2		
ε (Mn_4N)	0	100	0	400	10
ζ (Mn_3N_2—Mn_4N)	0—2	0—100	98—0	400—500	10—15
η (Mn_3N_2)	30—50	0	50—70	400	3—6
θ (Mn_6N_5)	100	0	0	400—550	1—3

Technetium nitrides. In work [384] technetium nitride was produced by heating NH_4TcO_4 in a stream of ammonia at a temperature of 700-1100°C. At 900-1100°C a new phase was detected, having a cubic face-centered lattice with a constant of a = 3,980-3,985 Å. The maximum nitrogen content corresponds to the composition $TcN_{0.76}$. The nitride of saturated composition corresponds to the formula TcN.

Rhenium nitrides. In a broad range of temperatures up to 2200°C it has not been possible to detect the interaction of rhenium with nitrogen [375, 376]. The formation of rhenium nitrides upon the thermal decomposition trivalent rhenium chlorammine at 350°C has also not been detected [377]. It was assumed that the formation of rhenium nitrides was possible by interacting rhenium oxide with ammonia [378]. Rhenium nitrides were first obtained by researchers [382], which first tried to produce nitrides by acting ammonia with rhenium at 200-1000°C which did not give the proper results, and then they prepared them by heating NH_4ReO_4 at 270-450° or $ReCl_3$ at 350-390°C in a stream of ammonia. The products formed by this had a composition between Re_2N (3.63% N) and Re_3N (2.45% N). Rhenium nitride Re_3N ($ReN_{0.34}$) was prepared in an analogous manner [380]. Authors [381] produced rhenium nitride by treating ammonium perrhenate with ammonia or nitrogen at 300-350°C for 20-25 h.

According to [383], the heating of rhenium powder in a stream of nitrogen at temperatures of 300-900°C for 4 h does not lead to the formation of rhenium nitrides. Whereas the interaction of rhenium with ammonia even at 250°C will form products, the nitrogen content in which increases with the increase in temperature, attaining upon a one-hour exposure at 600°C a value of 3.5% which corresponds the approximate composition of the nitride Re_2N. At practically all temperatures of the nitridation of rhenium powder of the nitrogen content is the greatest at the shortest exposures and drops with the increase in the nitridation time which is explained by the formation at short exposures of metastable products, which gradually convert to the form of stable nitrides.

Analogous results were obtained by investigating the interaction of ammonium perrhenate with ammonia; the formation of nitrides was observed at a temperature of 300°C.

Thus, it is possible to consider as established the presence in the rhenium-nitrogen system of two nitride phases – Re_3N and Re_2N.

Physical and chemical properties. Rhenium nitrides are black-colored powders, in external appearance not differing from the rhenium powder, obtained by reducing of the perrhenate with hydrogen. In a chemical regard the behavior of rhenium nitrides is analogous to the behavior of rhenium, but the nitride preparations are somewhat more inert. After a prolonged stay in humid air rhenium nitrides are oxidized to $HReO_4$. Water does not act on the nitrides. They readily dissolve in dilute HNO_3 and especially vigorously – in concentrated HNO_3. Heated concentrated H_2SO_4 slowly dissolves rhenium nitrides; HF and HCl do not act on them. With respect to oxygen and chlorine rhenium nitrides behave like metallic rhenium; in aqueous alkaline solutions they dissolve only in the presence of oxygen with the formation of perrhenates. They are not heat-resistant; when heated slowly in a vacuum decomposition starts even at 280°C. The nitride $ReN_{0.43}$ ($\approx Re_2N$) has a cubic face-centered lattice with $a = 3.92 \pm 0.002$ Å [382, 383]. The region of homogeneity of this

phase is not less than 2% nitrogen. The heat of formation is from -1 to -2 kcal/mole. It was determined that the nitride $ReN_{0.34}$ ($\sim Re_3N$) is a superconductor with a transition point of between 4 and 5°K [380].

6. Metal Nitrides of the Iron Family

Iron nitrides. The phase diagram of the iron-nitrogen system is shown in Fig. 86 [29, 396]. The solubility of nitrogen in α-iron at the eutectoid temperature is ∿0.10%;[8] with a reduction in temperature to 200°C the solubility decreases to ∿0.004%. The lattice of α-iron upon the dissolution in it of nitrogen is insignificantly expanded. The maximum solubility of nitrogen in γ-iron at a temperature of 600°C is 2.8%. At 585-590°C the γ-phase undergoes eutectoid disintegration ($\gamma \rightarrow \gamma' + \alpha$) with the formation of the γ'-phase.

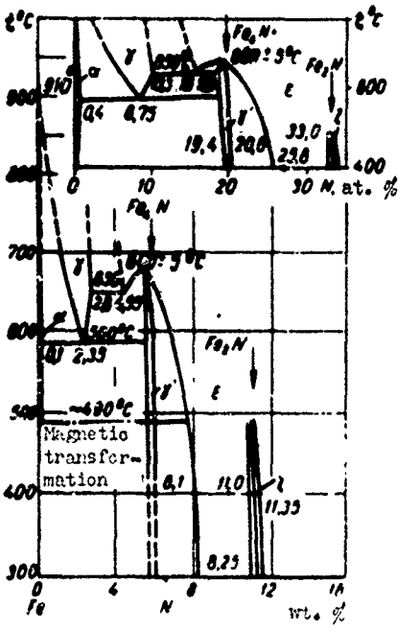

Fig. 86. Phase diagram of the iron-nitrogen system.

The γ'-phase (Fe_4N) has, as does the γ-phase, a face-centered cubic lattice with narrow limits of homogeneity of from 5.7 to 6.1 wt. % N; the space group is O_h^1.

The region of homogeneity of the γ'-phase at a temperature of 400°C is 5.64-6.14% N; at 500°C – 5.60-6.01% N; at 600°C – 5.51-5.90% N; at 680°C – 5.70-5.81% N [940].

The ε-phase, containing from 5.7 to 11.0 wt. % N, has a hexoagonal close-packed lattice with an ordered atomic arrangement of nitrogen. At 650°C it undergoes eutectoid disintegration to the γ- and γ'-phases.

The ξ-phase (Fe_2N) possesses a rhombic structure [387, 398] with an ordered atomic arrangement of nitrogen and a narrow region of homogeneity of from 11.0 to 11.35 wt. % N. The stoichiometric composition of the ξ-phase corresponds to 11.14% N.

It has been established that the ε-phase which was previously considered single-phase is a row of nitride phases with a compact hexagonal lattice of iron atoms and with a different atomic arrangement of nitrogen in the octahedral spacings [396-398]. The electron diffraction investigations of thin films of iron nitridation with ammonia on a chip of a rock salt crystal confirmed these assumptions [397, 947]. The presence of four hexagonal ε-phases has been established, one of which corresponds to the composition Fe_3N and three-to Fe_2N. The structures of the ε-phases can be described, if it is assumed that the basis is a compact hexagonal lattice constructed from the iron atoms with the constants a_m and c_m [146]. The nitride Fe_3N has a hexagonal lattice with the constants $a=a_m\sqrt{3}=2{,}76\sqrt{3}$ and $c=c_m=4{,}42$ Å. In the unit cell there 6 iron atoms and 2 nitrogen atoms; the space group is D_3^1. In Fig. 87 a projection of the crystal lattice of the nitride Fe_3N is given for plane (001). Within the limits of the cell the iron atoms are arranged in the projection plane and in the plane, passing at half of the height. One of the nitrogen atoms (1) lies in the plane, passing at 1/4 the height of the cell, the other (2) at 3/4 the height of the cell.

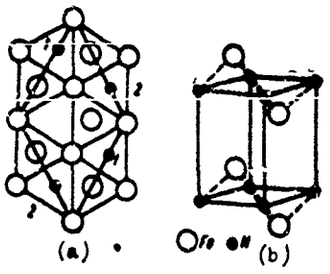

Fig. 87. Projection of the crystal lattice of the nitride Fe_3N for plane (001), (a) and the unit cell Fe_2N-ε (b).

The structure of the Fe_2N phase (the ε'-phase) differs from the structure of the Fe_3N phase only by the fact that in one of the planes (either at 1/4, or at 3/4 of the height of the cell) instead of one atom there are two nitrogen atoms.

Besides the nitride Fe_2N with a large unit cell the presence of two nitrides of the same composition with a small cell has been established ($a=a_m$ and $c=c_m$) [397]. One of them (the ε''-phase) has an ordered arrangement of nitrogen atoms, corresponding to a layer of the CdJ_2 lattice; the space group is D_{3d}^3 (Fig. 87a); in the second (the ε'''-phase) the nitrogen atoms are arranged in statistical disorder in the octahedral vacancies; the space group is D_{6h}^4; it is of the NiAs type. The degree of stability of the ε-phases has still not been established, it is possible that some of them are metastable compounds, formed as transition steps in the rearrangement of the nitrogen atoms.

Pinsker investigated by electron diffraction the cubic nitride Fe_4N [399, 400] and the degree of order in the iron nitride phases [401].

Physical properties. Iron nitrides, especially Fe_4N, noticeably dissociate at a temperature of 500°C [402]; the process of dissociation terminates at 1270-1527°C [403, 404]. The dissociation pressure of Fe_4N depending upon the temperature was studied in [405], and the kinetics of the elimination of nitrogen from the iron nitrides – in [406]. It was demonstrated that the activation energy upon the elimination of nitrogen from the γ'-phase is 42,100 ± 1400 kcal/mole at 350-500°C. The rate of elimination of nitrogen atoms is

expressed by an exponential dependence on temperature. The approximate calculation shows that about $1.8 \cdot 10^{-3}$ nitrogen atoms per 100 iron atoms are eliminated per second. Upon the isothermal decomposition of Fe_2N in a vacuum nitrogen is given off irreversibly, converting to Fe_3N and Fe_4N (this transition begins at 330°C) [407].

The nitride Fe_4N with hardening does not change, the ε-phase with a content above 7.5% N hardens without variations, and with a nitrogen content below 7.5% is unstable.

The nitride Fe_4N possesses strong magnetic properties (the average magnetic moment per molecule is 8.88). It is assumed that the iron in the nitride is not in ionic form, but in the form of "neutral atoms," joined by covalent bonds [408]. This assumption makes it possible to explain the nature of the magnetic properties of the nitride. Similar views were developed by Hume-Rothery, which considers that the introduction of nitrogen into the iron leads to the acceptance of a part of the iron electrons by the nitrogen atoms and the liberation of the corresponding 3d-states for the bond [409]. In this case an hexagonal close-packed structure of the alloys of iron with nitrogen appears.

The introduction of nitrogen into the iron causes a deceleration in the movement of the dislocations [410]. The hardness of the iron nitrides H_v fluctuates within a broad range from 224 to 687 kg/mm^2 [413]. The greatest hardness, apparently, is possessed by the ε-phase on the boundary with the $\varepsilon + \gamma'$ – field of the diagram. The physical properties of the iron nitrides were studied in [411-415]. In work [985] an X-ray spectral investigation of the phases Fe_4N and Fe_2N was conducted.

The physical properties of the iron nitrides are give in Table 76.

Table 76. Properties of iron nitrides.

Characteristic	γ'-Phase Fe_4N	ε-Phase (Fe_2N, ε', ε'', ε''' — Fe_4N)	ζ-Phase (Fe_2N)
Nitrogen content, wt. %	5,7—6	5,7—11,0	11,0—11,35
Crystal structure	Cubic face-centered	Hexagonal close-packed	Rhombic
Lattice constant, Å			
a	3,791—3,801 [396]*	2,660—2,764 [398]**	2,764 [398]***
b	—	—	4,829
c	—	4,343—4,420	4,425
c/a	—	1,683—1,599	—
Density, g/cm³			
calculated	7,21	—	7,08
pycnometric	6,57	—	6,35
Heat of formation, kcal/mole	2,6±2 [112, 47]	—	0,9±2 [47]
Effective magnetic moment per 1 atom of iron, Bohr magnetons	2,22 [451]	—	—
Curie point, °K	761 [452]	548 [453]	—

* In work [399] somewhat greater constant values are cited (3.81-3.97 Å), in work [940] a = 3.797 Å.

** According to [940], at 10.99% N for the ε phase a_0 = 4.787, c_0 = = 4.418 Å.

*** According to [940], for the ζ phase at 11.07% N a_0 = 5.525, b_0 = 4.827, c_0 = 4.422 Å.

Chemical properties. The nitride Fe_2N dissolves in dilute HCl; it is decomposed by chlorine and bromine, but does not give way to the action of iodine. The nitrides are decomposed by water [112]. With the action of carbon on iron nitride Fe_5C_2 will be formed at 400°C [454].

Production Methods. Nitrogen acts on iron extremely slowly, therefore the nitrides are usually produced by treating iron powder with ammonia. Thus, Fe_2N will be formed by the action of ammonia on powdered carbonyl iron at a temperature of 600-700°C. Researchers [63] to produce Fe_2N by treating iron with ammonia used a lower temperature — 350°C, in [398] — 450°C. Iron nitrides are also produced by the action of ammonia on thin films of vaporized on iron at 250-600°C [391]. The processes of the reaction diffusion of nitrogen in iron with the formation of nitrides were studied in [414, 415]. The peculiarities of the behavior of alloys of the iron-nitrogen system at high pressures were examined in [416].

In selecting the optimum conditions for producing iron nitrides it is necessary to consider the proximity of the temperatures of the occurrence of two processes — the formation of nitrides ($2xFe + 2NH_3 \rightarrow 2Fe_xN + 3H_2$) and their dissociation ($2Fe_xN \rightarrow 2xFe + N_2$) [414].

The lowest iron nitrides will be formed upon heating the highest nitrides in a vacuum, for example, Fe_2N when heated to 440-600°C, converts to Fe_4N.

The authors [274] produced the iron nitride Fe_2N by thermal decomposition $(NH_4)_3FeF_6$ in a stream of ammonia at a temperature of 600°C.

In connection with the high properties of nitridation layers on iron, steels and cast iron, and also with the role of nitrogen in steels in numerous works questions of the nitridation of iron and its alloys were investigated both from the scientific, and also from the industrial aspect [402, 447].

Cobalt nitrides. The solubility of nitrogen in α-cobalt at a temperature of 600°C is about 0.6 wt. %. In the cobalt-nitrogen system the existence of two nitrides was detected – Co_3N and Co_2N [29, 455, 458]. The region of homogeneity of the nitride Co_3N lies within the limits of from 7.7 to 8.0 wt. % N. The Co_3N has a hexagonal lattice. The nitride Co_2N is isomorphic to Co_2C [456]; it has rhombic distorted hexagonal packing of the metallic atoms. The arrangement of the interstitial atoms of nitrogen for Co_2N is the same as for Fe_2N.

Physical and chemical properties. Both nitrides have a color from gray to black; they yield poorly to the action of weak acids in the cold; concentrated H_2SO_4 dissolves them slowly; in concentrated hydrochloric and nitric they dissolve rapidly. When heated both nitrides dissolve rapidly in dilute mineral acids. The physical properties of cobalt nitrides are presented in Table 77.

Table 77. Properties of cobalt nitrides.

Characteristic	Co_3N	Co_2N
Nitrogen content, wt. %	7,34	10,71
Crystal structure	Hexagonal	Rhombic
Lattice constant, Å:		
a	2,658 [455]	2,842 [455]
b	—	4,627
c	4,531	4,330
c/a	1,71	—
Density, g/cm³	7,1	6,3
Heat of formation, kcal/mole	~—2 [460]	—

Production methods. Nitrogen acts slowly on cobalt, therefore nitridation is carried out with ammonia with the formation at a temperature of 250-300°C of the nitride Co_3N, and at 380-500°C – of Co_2N. Cobalt nitrides are also produced by the heating at 2000°C cobalt cyanamide $Co(CN)_2$ and its mixture with cobalt oxide in a nitrogen medium [6]. In work [457] cobalt nitrides were produced by the thermal decomposition in a vacuum of cobalt amide $Co(NH_2)_3$ with the liberation with this of ammonia. Depending upon the temperature of decomposition either nitrides at 50-70°C or slightly concentrated solid solutions of nitrogen in cobalt will be formed at 220-250°C.

Upon treating the oxide Co_3C_4 with ammonia at 330-390°C for 2-3 h the formation not of nitrides, but of cobalt hydroxy-nitrides occurs [455].

Cobalt nitrides can be produced by nitriding CoF_2 at 360°C. The Co_3N is usually formed by the thermal decomposition of Co_2N at 276°C [455].

Nickel nitrides. According to [459], the solubility of nitrogen in nickel does not exceed 0.32% (with the simultaneous dissolution of 0.17% hydrogen, liberated upon nitriding with ammonia).[9] According to more reliable data [458] at 450°C only 0.07% N is dissolved in nickel. The X-ray diffraction analysis revealed the existence in the nickel-nitrogen system of only one nickel nitride – Ni_3N, having an hexagonal lattice of metallic atoms with the arrangement in the interstices of nitrogen atoms. The nitride Ni_3N decomposes above 360°C; at 440°C the process of decomposition occurs very rapidly [458].

Physical and chemical properties. Nickel nitride Ni_3N is a dark-gray-colored substance. The lattice constants of Ni_3N (7.37 wt. % N) are a = 2.670, c = 4.307 Å, c/a = 1.613 [458]; the specific gravity is 7.66 g/cm^3; the heat of formation of nickel nitride Ni_3N from the elements – 0.2 ± 0.1 kcal/mole [460]. The nitride Ni_3N is stable in sodium hydroxide; it is slowly decomposed by 2N hydrochloric,

sulfuric and phosphoric acids in the cold; concentrated H_2SO_4 does not decompose it, concentrated HCl and HNO_3 in the cold decompose it violently. When heated it interacts energetically (in the cold) and exposively (with heating) with concentrated and dilute mineral acids; sulfuric acid acts on it more slowly and more tranquilly than the others. When dissolved in dilute acids not containing oxygen hydrogen is liberated which is connected with the transition of nickel to the bivalent state. Concentrated H_2SO_4 when heated is reduced by the nitride to SO_2, and dilute – to H_2S [458]. In air the nitride at a temperature of 800°C burns to NiO.

Production methods. Nitrogen in a broad temperature range, at least up to 900-1400°C, does not act on nickel, therefore the preparation of nickel nitrides is accomplished by heating powdered nickel in an ammonia medium at a temperature of 440-450°C, or by heating complex halides – $NiF_2 \cdot 2NH_4F$ in a stream of ammonia at 390-410°C. Nickel nitrides are also obtained by heating $NiBr_2$ in a stream of ammonia, from which by the action of ammonia there will first be formed an ammoniate, which at 450°C decomposes with the production of Ni_3N [458]. In work [461] the interaction of fine nickel powder (obtained by the reduction of oxalate at 600°C) with ammonia was in detail investigated. The dependence of the nitrogen content in the nickel on the rate of the stream of ammonia was shown; the intense catalytical action of the addition of 1% Fe to the process of nitriding nickel was detected. The optimum reaction temperature was 300°C, the rate of the stream of ammonia was 40 ml/min; the reaction time was 10-20 h; the obtained product contains 7.3-7.4% N.

It is also possible to prepare Ni_3N by heating $Ni(CN)_2$ in a nitrogen medium at a temperature of 2000°C [6].

In work [462] the method of producing alloys of nickel and cobalt nitrides is described and data on the magnetic properties and the hardenss of these alloys are given.

7. Platinoid Nitrides

There is practically no information about compounds of platinoids with nitrogen [463, 464, 6, 29]. It is only known that in an investigation of the interaction of palladium with nitrogen, no dissolution of nitrogen in Pd was detected up to 1400°C [29]. However in a vacuum analysis of certain platinoids insignificant admixtures of nitrogen (in Rh - 0.0003%; in Ru - from <0.002 to 0.0118% [465]. In the survey [156] it is indicated that a small quantity of palladium nitride will be formed in the arc between palladium electrodes in a nitrogen medium.

8. Actinide Nitrides

Thorium nitrides. Previously it was considered [121, 483, 493], that thorium forms one nitride Th_3N_4, existing in two variants, differing in structure, properties and color (one is yellow, the other is brown in color). It was assumed that the brown nitride was an individual compound of the composition Th_2N_3 [493].

At the present time it has been clearly established that thorium forms three nitrides - ThN, Th_2N_3 and Th_3N_4 [43, 495-497].

The solubility of nitrogen in thorium, according to [498], increases from 0.05 wt. % N (0.8 at. % N) at 845°C up to 0.35 wt. % N (5.2 at. % N) at 1490°C. In this range solubility can be represented by the equation

$$\lg C = -\frac{2405}{T} + 0{,}9115.$$

where C is the nitrogen concentration, wt. %.

The temperature dependences of the reaction of nitridation and of the coefficient of diffusion have been established

$$k = 5{,}9 \cdot \exp(-24300/RT) \ [\text{m}l/\text{cm}^2 \cdot \text{s}],$$

$$D = 2{,}1 \cdot 10^{-3} \cdot \exp(-22500/RT) \ [\text{cm}^2/\text{s}].$$

The nitride ThN has a cubic lattice of the NaCl type, and Th_2N_3 - hexagonal lattice.

Physical and chemical properties. The thorium nitride ThN has a high melting point; it is stable at high temperatures in a vacuum. The thorium nitride Th_3N_4 is unstable in a vacuum at 1500°; in a nitrogen medium it is stable at 1730°C. The Th_2N_3 decomposes in a vacuum, forming ThN [496].

Properties of the Th_3N_4 phase have been little studied [996]; its crystal structure has been basically investigated [1022]. According to these data, Th_3N_4 has a rhombohedral lattice with a = 9.398 Å, α = 23.78° (the constants of the respective hexagonal lattice are: a = 3.871, c = 27.385 Å); the calculated density is 10.55 g/cm^3.

The ThN is yellow-colored; it is stable with respect to acids. Brown Th_2N_3 is readily hydrolyzed by water or atmospheric moisture [493, 623]. Both nitrides at room temperature react slowly with oxygen, forming ThO_2 [497]. The properties of the thorium nitrides are given in Table 78.

Production methods. The thorium nitrides are usually obtained by treating throium with ammonia or by the action of ammonia on thorium hydride [493]. In the latter case at a temperature of 1000°C Th_2N_3 will be formed. The thorium nitrides will be formed by the direct nitridation of the metal with dry, purified nitrogen at 800°C for 3 h [24].

Thorium nitride can be produced by the accumulation method from the gaseous phase, for example on a tungsten filament, heated to 1000°C in a mixture of $ThCl_4$ with $N_2 + H_2$ [24].

Information exists about the possibility of forming of thorium nitrides by interacting thorium carbide with ammonia and ammonia with thorium chloride, and also by the thermal decomposition of the thorium amides $Th(NH_2)_4$ and $Th(NH)_2$ [493].

Table 78. Properties of thorium nitrides.

Characteristic	ThN	Th_2N_3
Nitrogen content, wt. %	5.69	8.30
Crystal structure	Cubic face-centered NaCl type	Hexagonal La_2O_3 type
Lattice constants, Å:		
a	5.20 [494] - 5.144 [93]	3.875 [495]
c	-	6.175
c/a	-	1.595
Density, g/cm^3	11.50	10.51
Melting point, °C	2790 ± 30 [1019]	2100 [499]*
Heat of formation, kcal/mole	90.6 [996]	309.5 ± 4.0 [47]*
Entropy, cal/deg·mole	23.5 [996]	42.7 ± 2.5 [47]*
Dissociation pressure	$\lg P$ (at.) = $= 8.086-33.24/T^{-1} + + 0.958\cdot10^{-17}T^5$ [1019]	88 mm Hg at 2230°C [496]
Transition point to the superconductive state	-	<1.2 [275, 304]*

*For Th_3N_4.

Protactinium nitrides. Protactinium nitride is ascribed the composition PaN_2 [493]. The PaN_2 is a light-yellow solid compound, formed by the action of ammonia on $PaCl_5$ or $PaCl_4$ at a temperature of 800°C; it has the same structure as UN_2.

Uranium nitrides. The uranium-nitrogen system has been repeatedly investigated, especially during the last 20 years [500]. The existence of three uranium compounds with nitrogen has been established - the mononitride UN, the sesquinitride U_2N_3 and the dinitride UN_2. The region between UN and U_2N_3 is two-phase; U_2N_3 with an increase in the nitrogen content converts to the nitride UN_2, i.e., the region among these two compounds is a region of homogeneous solid solution. The investigation of the system was continued in work [501], where technological recommendations for

producing the individual nitrides are given, especially in the molten state. In this work phase diagram of the U-N system for several nitrogen pressures are plotted (Fig. 88).

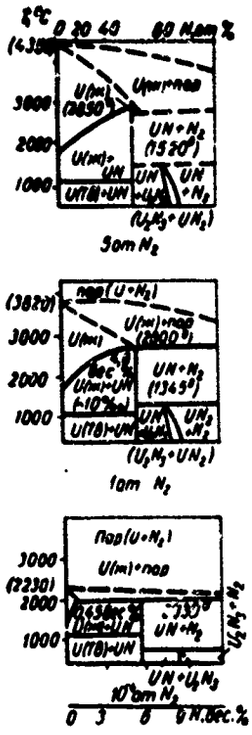

Fig. 88. Phase diagram of the uranium-nitrogen system for various nitrogen pressures. Designations: ат % = at. %; вес. % = wt. %; пар = pair.

The most complete investigation of the system was made in work [502], the results of which are given in the form of a phase diagram of the U-N system for a nitrogen pressure of 5 at. (Fig. 89).

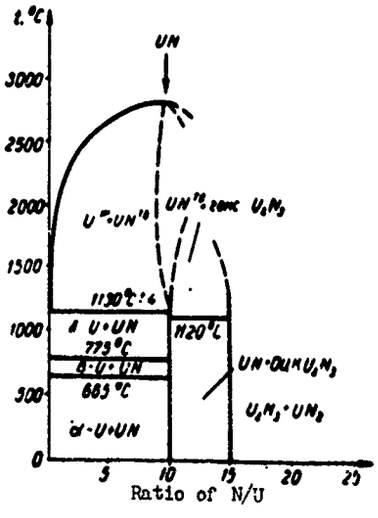

Fig. 89. Phase diagram of the uranium-nitrogen system (p_{N_2} = 5 at.).
Designation: гекс = hexagonal.

The solubility of nitrogen in uranium is small [497].

Uranium monotride has a cubic face-centered lattice of the NaCl type; it melts congruently at a temperature of 2835 ± 30°C (the ratio of N:U = 0.96 ± 0.03). Uranium sesquinitride U_2N_3, according to [500, 503], is a cubic body-centered lattice of the Mn_2O_3 ($D5_3$) type, according to [43] - a hexagonal lattice of the Th_2S_3 type. Now it has been proved [502] that both data are correct, because the nitride undergoes at 1315°C polymorphic transformation, being converted from a cubic, body-centered lattice to a hexagonal lattice. Uranium dinitride UN_2 has a cubic face-centered lattice of the CaF_2 type. The phase diagram of the U-N system has also been plotted in [516, 1004].

Physical properties. Uranium mononitride is a refractory compound with a melting point of 2835°C (with respect to the old data of Chiottii [43] - 2650°C, according to [504] - 2850°C at a nitrogen pressure of more than 2.5 at.). At lower pressures incongruent melting occurs with the decomposition into liquid uranium, saturated with nitrogen, and gaseous nitrogen. The dissociation pressure is expressed by the equation [504]

$$\lg p = [illegible] - (29.54 \cdot 10^3)T^{-1} + (5.57 \cdot 10^{-15})T^5.$$

Uranium nitride UN, contaminated by oxygen, decomposes at higher temperatures than pure nitride. The cubic structure of this nitride was confirmed by the neutron-diffraction method [505].

By the irradiating uranium mononitride with neutrons it was established that the effect of the transformation of nitrogen into hydrogen and carbon was insignificantly small [506]. The basic effect is uranium fission, entering into the nitride.

The data obtained by irradiating uranium mononitride with neutrons are presented in Table 79.

Table 79. The effect of neutron irradiation on uranium mononitride.*

Uranium enrichment, %	Uranium burn out, %	Maximum temperature on the surface, °C	Decrease in density, %
0.22	0.1	65-70	0.73-1.6
0.72	0.4	100-105	1.1-2.1
5	2-3.5	275-580	2.3-6.4

*Samples with a shell of stainless steel of brand 304 or without a shell were investigated. Samples without a shell are destroyed, and they remain in the shell without changes.

In work [964] single-crystals of uranium mononitride with a density of 99-100.1% of the rated were prepared by arc smelting. Their hardness, according to Knup, was equal to 555, according to Vickers - 500. The temperature of congruent smelting at a nitrogen pressure of 2.5 at. was equal to 2850 ± 50°C.

According to [1012], where the thermal conductivity of uranium mononitride was measured at temperatures of 900-1650°C, above 1200°C the thermal conductivity does not depend on temperature and is at 1650°C about 0.26 W/cm × s. In this temperature range the electron component of thermal conductivity prevails, for example, at 1300°C it is up to 80%.

The electrophysical properties of uranium nitrides were investigated in work [507], in particular - the temperature dependence of electrical conductivity (Fig. 90) and thermo-emf (Fig. 91) of the mononitride, the same - for dinitride (Fig. 92) and the thermo-emf for nitrides with a different ratio of nitrogen and uranium content (Fig. 93). The high values of thermo-emf can be used under certain conditions for thermoelectric current generators. The mononitride has p-type conductivity. The magnetic susceptibility of the mononitride, equal, according to these data, to $3050 \cdot 10^{-6}$, can be explained by the presence of two unpaired 6d-electrons (the theoretical value for the two unpaired 6d-electrons is $3333 \cdot 10^{-6}$) and by the participation of one 6d-electron per uranium atom in the Me-Me bond.

The negative temperature coefficient of electrical conductivity is caused by carrier scattering with temperature. At low temperatures these carriers can be provided by the Me-Me compound, and at high temperatures excitation of the carriers within limits of the bands, pertaining to the U-N bonds. The author [507] considers that the relatively large difference in the electronegativities of the UN components, consisting of 1.5, can cause the presence of a large energy gap which causes the delivery of a certain number of current carriers at low temperatures. For UN_{2-x} nitride phases an n-type conductivity has been established; the low values of conductivity with high carrier concentration which corresponds to x = 0.41, can be ascribed to the low mobility of the carriers. It is possible to expect that UN_2, being a less ionic compound than uranium dioxide which is isomorphic to it (the difference in the electronegativities is 2.0), has a higher mobility of carriers than the 10 $cm^2 \cdot V \cdot s$, established for UO_2.

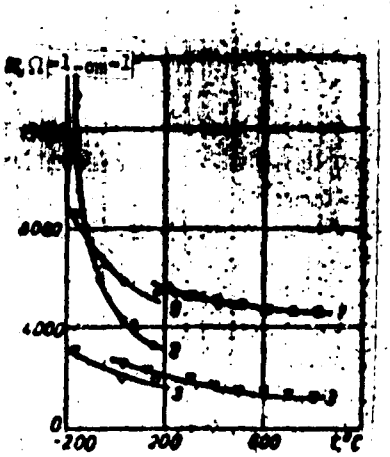

Fig. 90. The temperature dependence of the electrical conductivity of the nitride UN. 1 – 1.08% C; 2 – 0.2% C; 3 – 0.06% C.

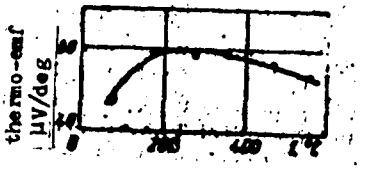

Fig. 91. The temperature dependence of the thermo-emf of UN.

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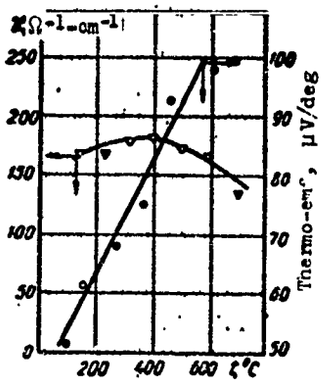

Fig. 92. The temperature dependence of electrical conductivity and thermo-emf of UN_2.

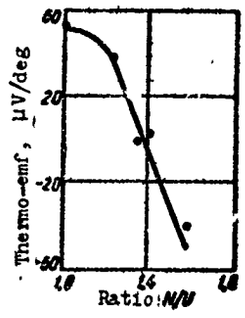

Fig. 93. The dependence of thermo-emf on the ratio of N/U.

At a certain value of x, greater than 0.41, the phase transition of UN_2 from a CaF_2 structural type to a La_2O_3 structural type occurs. Uranium sesquinitride has as compared to the high-conductive mononitride low electrical conductivity and simultaneously a small value of thermo-emf. It is assumed that U_2N_3 can have only a stoichiometric composition.

The electrical conductivity and thermo-emf of uranium mononitride at low and average temperatures were measured in work [831]. In Fig. 94 the dependence of electrical resistance on temperature is shown, and in Fig. 95 - thermo-emf (with respect to copper).

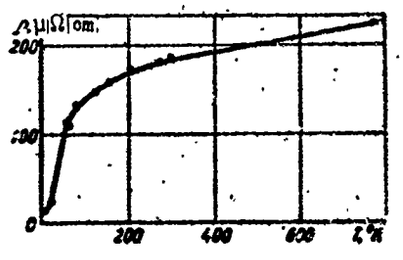

Fig. 94. The temperature dependence of the electrical resistance of UN.

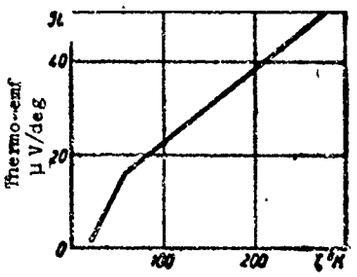

Fig. 95. The temperature dependence of thermo-emf of UN.

A more detailed investigation of the magnetic properties of uranium nitrides was made in the works of Tzhebyatovskiy with his colleagues [508, 509]. It was demonstrated that in uranium mononitride the high negative Weiss constant (-310) indicates a strictly antiferromagnetic combination of electron spins. This coincides with the shortest interatomic distance of U-U in this compound with nitrogen, equal to 3.449 Å. The β-U_2N_3 phase (the hexagonal variant) is characterized by ferromagnetic properties at low temperatures in the metastable state tempered from a high temperature; the Curie point is equal to +186°K. The α-U_2N_3 phase (the cubic variant) has a magnetic moment of 1.92 Bohr magnetons; to explain this value it is possible to assume that part of the uranium atoms is in the U^{4+} ionic state (μU^{4+} = 2.83 Bohr magnetons), and with them part of the diamagnetic ions U^{6+}: $U^{4+}_{1.5}$ $U^{6+}_{0.5}$ N^{3-}_3, or there is a mixture of tetra- and pentavalent uranium ions: U^{4+} 1.0 + U^{5+} 1.0 U^{3-} 3.

The nitride U_2N_3 at temperatures of 700-800°C in a vacuum gives off nitrogen up to 1300°C, at this temperature and low pressures it decomposes to the mononitride and nitrogen, and at high temperatures - to the mono- and dinitride [500]. In the latter case the alloy volume decreases by 13%. The heat of decomposition of $U_2N_3 \rightarrow UN + N_2$ is equal to 57-58 kcal/mole of N_2 [963].

In work [1055] data are given on measuring the equilibrium pressure of the nitride, carbonitride phases of uranium depending on pressure and temperature and the enthalpy and entropy of these phases were calculated, and also the parameters of the hexagonal lattice of the β-U_2N_3 (a = 3.698, c = 5.839 Å).

The physical properties of uranium nitrides are given in Table 80.

Table 80. Properties of uranium nitrides.

Characteristic	UN	α-U_2N_3	β-U_2N_3	UN_2
Nitrogen content, wt. %	5.55	8.22	8.22	10.5
Crystal structure	Cubic face-centered	Cubic body-centered	Hexagonal	Cubic face-centered
Lattice constant, Å:				
a	4,800 [500]	10.678 [500]	3.69 [511]	5.31 [500]
c	-	-	5.83	-
c/a	-	-	1.58	-
Density, g/cm^3	14.32 [500]	11.24 [500]	12.44 [508]	11.73 [514]
Melting point, °C	2850 ± 50 [964]	-		-
Heat of formation from the elements, kcal/mole	68.5 [47]	256 [9]		-
Entropy, cal/deg·mole	12.5 [47]	-		-
Region of stable existence, °C at a N_2 pressure of 5 at.	-	1520 [501]		-
" " " 1 at.	-	1345		-
" " " 10^{-4} at.	-	780		-
Thermal conductivity cal/s·cm·deg	0.0325 [507]	-		-
Electrical conductivity $a^{-1}.cm^{-1}$	3200 [507]	-		-
Thermo-emf μV/deg	57 [507]	-		-
Magnetic susceptibility	$3050 \cdot 10^{-6}$ [507]	See [503, 509]		-
Transition temperature in the superconductive state °K	<1.20 [275, 304]	-		-
Coefficient of thermal expansion $\alpha \cdot 10^6$ (at 20-1600°C)	10.1 [976]	-		-
Elastic modulus, kg/cm^2	$2.2\text{-}2.5 \cdot 10^5$ [976]	-		-
Shear modulus, kg/cm^2	$0.3\text{-}1.10^3$ [976]	-		-
Poisson's ratio	0.1-0.26 [976]	-		-
Hardness (according to Knup), kg/mm^2	600-700 [976]	-		-

Chemical properties. An important property of the uranium nitrides is their ability to actively absorb gases which is used for purifying nitrogen of oxygen and moisture and makes it possible in certain cases to use the uranium nitrides as getters. Upon the oxidation of sintered uranium mononitride in oxygen at temperatures of 350-480°C and pressures of up to 1 at, a number of intermediate oxides between U_3O_8 and UO_3 will be formed. The activation energy of oxidation in the indicated temperature interval is 24.5 kcal/mole [510, 969].

In work [962] it was demonstrated that the oxidation of uranium mononitride with oxygen, CO_2, and air, saturated with moisture, is expressed by the linear kinetic law with an activation energy of from 10.4 to 15.4 kcal/mole. The oxidation product at 300°C consists mainly of U_3O_8. Corrosion by water at 100°C and sodium-potassium alloy at 820°C occurs very slowly. On the whole, uranium nitrides oxidize readily in air, are not to soluble in acids and alkaline solutions [514], but are readily decomposed by molten alkalis. The highest uranium nitrides are reduced by hydrogen.

In work [43] the high resistance of uranium nitride to the action of tantalum and thorium nitrides at 2000°C was shown. The high melting point of the mononitride makes it possible using it for refractory articles, exploited in nitrogen or inert gaseous media.

Obtaining methods. Uranium nitrides are usually prepared by nitriding uranium or uranium hydride.

A study of the nitridation reactions of uranium was made in [511, 512]. At nitridation temperatures of 650-900°C in the diffusion layers three phases have been detected - a mononitride, a dinitride, and also a hexagonal variant of the sesquinitride. In the layers, produced [512] by the nitridation of uranium at 550-750°C there is also mainly detected the nitride UN_2 with minor admixtures of U_2N_3. At nitridation temperatures of between 775 and 900°C, as in [511].

all three nitride phases were detected. The nitridation rate of uranium in both indicated temperature ranges obeys the parabolic law, however the diffusion rate and the activation energies are different

$$D = 202 \cdot \exp(-25500/RT) \text{ at } 550-750°C,$$

$$D = 3{,}95 \cdot \exp(-15100/RT) \text{ at } 775-990°C.$$

The variation in the parameters of diffusion is connected with β → γ-transformation of metallic uranium (according to new data [502], the transformation occurs at 771-778°C).

Activation energies of the nitration process have been established equal at 630°C to 16 kcal/mole, and at higher temperatures - to 7 kcal/mole (the temperature of the β → γ-transformation of uranium); this indicates a far-reaching analogy between the interaction mechanism of uranium with nitrogen and oxygen [515].

In work [522] the nitration of uranium powder obtained by calcium-thermal reduction in temperature range of 300-700°C at a nitrogen pressure of 50-700 mm Hg was investigated. The particles of uranium powder had a spherical shape with dimensions of 2-200 μ. In the first stages of the reaction UN is produced, and at 600°C after 30 min the reaction is terminated with the formation of a product, close in composition to U_2N_3. The activation energy of the process at 500-700°C is equal to 27 ± 2 kcal/mole which agrees well with the value, determined in [512]. In the nitration process of the uranium particles are pulverized which leads to the exposure of new surfaces and to the acceleration of the nitridation process. Before the onset of the grain destruction process the reaction proceeds not according to parabolic law, but according to the law of the $\Delta m = kt^n$ type, where n is close to 1/3.

The minimum nitrogen pressure, required to produce cast UN, should be 2.5 at. At lower pressures it is impossible to attain

saturation of the uranium liquid phase with nitrogen before producing the composition UN. The production of UN is possible by the decomposition of U_2N_3 at low temperatures in a pumped system, in which the required vacuum is maintained. However in as much as the rate of the process at low temperatures is small, the minimum temperature of this method of producing uranium nitride is 1000°C. Higher temperatures impair the vacuum conditions, necessary for decomposition.

In nitriding uranium under very great pressure of the order of 120-130 at. A mixture of uranium mono- and dinitride is formed with an overall nitrogen content in the alloys of up to 55-66 at. %.

Chiotti [43] prepared uranium mononitride by passing nitrogen, ammonia over uranium shavings at temperatures of 400-940°C. Nitrogen was thoroughly purified also by passing it over uranium shavings at 500°C. Under the conditions selected by Chiotti mixtures of the nitride phases of uranium were obtained, the transition of which to the heat-resistant mononitride was produced by heating the nitridation products in a vacuum at a temperature of about 1500°C.

The nitridation of metallic uranium with ammonia was again investigated in [987]. In the temperature interval 470-1000°C (at a pressure of 1 at) products of compositions respectively from $UN_{1.74}$ to $UN_{1.55}$. All the nitride phases of UN_x with $x \geq 1.50$ had a cubic BCC-structure [body-centered cubic structure] of the Mn_2O_3 type with a gradual transition with an increase in value of x to CFC-structure [cubic face-centered structure] of the CaF_2 type, characteristic for UN_2.

Researchers [500] produced uranium nitrides by interacting uranium hydride with ammonia at a temperature of 200°C or with nitrogen at 350°C under conditions of thoroughly isolating oxygen

from getting into the reaction space. In work [485] a method of producing uranium nitride with an intermediate stage of the formation of uranium hydride is recommended. Pieces of uranium are first hydrogenated at a temperature of 200°C, then nitridation (2-3 kg/cm^2). By a high speed reaction products will be formed, having the composition UN_x, with x = 1.77-1.78, i.e., being a mixture of U_2N_3-UN_2. Upon heating this product for several hours in a vacuum at 800°C uranium mononitride is obtained.

The purest uranium mononitride is produced by arc smelting uranium in a nitrogen medium at high temperatures [513].

Uranium nitride, to which is ascribed the composition U_3N_4 (a mixture of phases) will be formed by interacting UF_4 with ammonia at 800°C [274], or UCl_4 with ammonia [514].

Articles of uranium mononitride are usually prepared by methods of powder metallurgy. For example, in [43] articles of a powder with a particle coarseness of 100 meshes were produced by pressing the intermediate products under a pressure of 3.1-3.7 t/cm^2 with subsequent sintering at a temperature of 2000-2100°C. Such articles have a porosity of 16%; the linear shrinkage upon sintering is about 3%. The porosity of articles of large dimensions fluctuates within the limits of 23-30%. An analysis of the material of the articles after sintering shows the closeness of its composition to uranium mononitride with a certain deficit in the nitrogen content. In an attempt to manufacture crucibles from mixtures of U_2N_3 with metallic uranium, composed taking into account the formation of the mononitride, the intermediate products during sintering were warped and cracked. Sintering in both cases was carried out in a high-frequency induction furnace.

The conditions for preparing of articles of uranium mononitride were studied in [513]. The articles were produced by the method

of hot pressing in graphite molds at temperatures of 1370-1678°C, and pressures of 200-400 kg/cm^2 for 30 min. The articles obtained after 18 min of sintering have a low density (about 80%), which can be further increased by ~10% by subsequent sintering at 1700°C for 2 h, and also by refining the mononitride particles. The contamination of the articles with carbon as a result of the contact with the graphite mold is small and constitutes a maximum of 0.44 wt. %. The oxygen content substantially decreases as compared to the original powder and is in the article 0.06 wt. % (see also [1080]).

According to [507], articles of UN are also prepared by the hot pressing method at a temperature of 1800°C for 15 min; their density was 10.3 g/cm^3, the carbon impurity was 0.06%, and oxygen - 0.13%.

In connection with the perspective use of uranium mononitride as nuclear fuel its production, properties and methods of preparing articles from it are covered by extensive literature, summaries of which are given in the detailed survey [976], and also in the bibliography [977].

Neptunium nitrides. Neptunium nitride NpN has a cubic structure of the NaCl type with a lattice constant of a = 4.8987 Å [495, 1005]. It is produced by interacting of neptunium hydride with ammonia at a temperature of 750-800°C [517, 496]. Upon heating neptunium tetrachloride with ammonia within the limits of 350-1000°C nitride of neptunium will not be formed.

An investigation of the decomposition reaction NpN(solid) → → Np(gas) + 0.5N_2(gas) at 2210-2830° showed [1005] that the vapor pressure obeys the equation

$$\lg p\ (\text{at}) = 8{,}193 - \frac{29{,}54 \cdot 10^3}{T} + 7{,}87 \cdot 10^{-6} T^2 \ldots$$

The NpN melts congruently at 2830 ± 30°C at a nitrogen pressure of up to 10 at.

The NpN does not dissolve in water; it is soluble in hydrochloric acid [517].

Plutonium nitrides [1028]. Plutonium forms one nitride PuN [518]. According to Zachariasen [495, 519], PuN has a cubic face-centered grid with a constant (for the composition $PuN_{0.907}$) a = 4.9069 Å, varying linearly with temperature: $a = 4.9069 (1 + 12.29 \cdot 10^{-6} t)$ Å, where $20 < t < 900°C$.

The density of the nitride is 14.23 g/cm^3; the free energy of the formation of PuN at 700°K is equal to -60 ± 1 kcal/mole; at 298°K it is more negative than -70 kcal/mole [997]; the entropy of formation from the elements is $\Delta S°_{298} = -22 \pm 1$ cal/deg·mole. The melting point of plutonium mononitride is equal to 2750 ± 75°C. It begins to intensively vaporize at 1600°C with disproportionation according to the reaction $PuN_{1-x} \rightarrow Pu + (1-x)PuN$. The dissociation pressure according to the reaction PuN(solid) → Pu(liq) + 0.5N_2(gas) in the range 2290-2770°C is determined by the equation

$$\lg p\,(\text{at}) = -\frac{29540}{T} + 11.28 \lg T - 7^{*} + 8.193.$$

The coefficient of thermal expansion of PuN according to the results of dilatometric measurements is equal to $9.30 \cdot 10^{-6}$ deg^{-1}, and according to the roentgenographic method $12.29\text{-}13.80 \cdot 10^{-6}$ deg^{-1}.

Zachariasen ascribes semimetallic properties to plutonium nitride. In work [831] the electrical resistance and the thermo-emf were determined of PuN at low and average temperatures (Figs. 96, 97), which in general confirm this assumption.

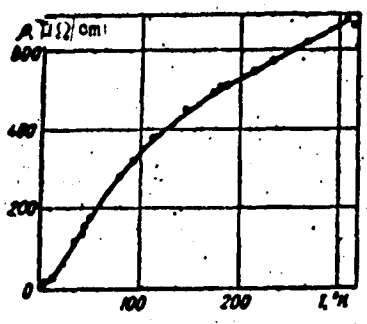

Fig. 96. The temperature dependence of the electrical resistance of PuN.

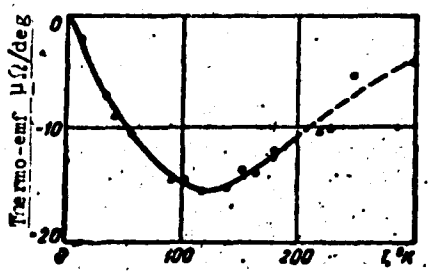

Fig. 97. Temperature dependence of thermo-emf of PuN.

Plutonium mononitride is a dense and fragile substance with a black color; it is unstable in humid air and oxygen. Under the effect of humid air it hydrolyzes according to the reaction [496]:

$$PuN + 2H_2O \rightarrow PuO_2 + NH_3 + {}^1/_2 H_2.$$

In cold water PuN hydrolyzes slowly, and in hot - very rapidly with the formation of $Pu(OH)_4$.

In hydrochloric and phosphoric acids the nitride dissolves rapidly, somewhat more slowly - in nitric acid, still more slowly - in hydrofluoric and nitric. Upon dissolution in hydrochloric and sulfuric acids in the cold trivalent plutonium salts will be formed.

Oxidation with oxygen occurs intensively beginning at 500 and especially rapidly - at 1000°C.

Nitrogen acts very slowly on plutonium both at low temperatures, and also at 800-1000°C [518]. Therefore plutonium nitride is usually obtained by the action of ammonia both on plutonium, and also on its compounds: by acting ammonia on plutonium at 1000°C; by interacting plutonium trichloride with ammonia at 800-900°C; by acting ammonia at a pressure of 250 mm with plutonium hydride at 600°C with subsequent slow cooling to room temperature [493, 520]. A modification of the latter method is that described in [824] the production of PuN by heating plutonium hydride in a nitrogen medium at temperatures above 230°C.

The authors [485] prepared plutonium nitride by hydrogenating the surface of pieces of plutonium at a temperature of 200°C with the subsequent treatment with nitrogen at 250°C. The nitridation proceeds at great speed. The lattice constant a of the nitride, produced in this was then annealed at a temperature of 1000-1500°C, is equal to 4.912 Å. It is indicated that with an increase in the annealing temperature the lattice constant increases somewhat which attests to the partial loss of nitrogen.

In an attempt to produce PuN by the arc smelting method [521] mixtures of PuN, PuO_2 and free plutonium will be formed. The product vaporizes at a temperature of 2650°C in helium without fusion.

Detailed data about the methods of producing and the properties of uranium and plutonium nitrides are also given in the report [1041].

Footnotes

[1]Obtained by extrapolation.

[2]According to [978], the magnetic susceptibility is $37 \cdot 10^{-6}$.

[3]Somewhat different data concerning the temperatures of the chloridization of titanium nitride are cited in work [230].

[4]Not considering the formation of phases of variable composition and various thickness.

[5]The kinetics of the nitrogen loss by solid solutions of the nitrogen in the niobium was also investigated in work [981].

[6]According to [939], chromium at 1600°C and a pressure of N_2 = 1 at. dissolves 6.5 wt. % of nitrogen (in a supercooled liquid state).

[7]With respect to the antiferromagnetism of chromium nitrides see also [331].

[8]According to [940], the solubility of nitrogen in α-iron is at the eutectoid temperature 0.115%; according to [941] – 0.095%, according to [942] – 0.108%. The solubility of nitrogen in molten iron at 1600°C and a pressure of N_2 = 1 at. is 0.0438 ± 0.0007 wt. % [939].

[9]The solubility of nitrogen in liquid Ni at 1600°C and at a pressure of N_2 = 1 at. is equal to 0.001 ± 0.001 wt. % [939].

C H A P T E R VI

NITRIDES OF ELEMENTS OF THE BORON SUBGROUP

1. Boron Nitrides

The Boron BN nitride, discovered more than one hundred years ago by Balmain [625], is known in three modifications — α-BN (hexagonal), β-BN (cubic) and γ-BN (hexagonal close-packed).

The α-BN has a hexagonal crystal structure similar to the structure of graphite. It consists of graphite-like layers located in contrast to the structure of graphite exactly under each other with an alternating of the atoms of the boron and nitrogen along the z axis (Fig. 98a). The space group is $C6m2(D_{3h}^{1})$, Z = 2 [36, 626]. Due to proximity of the structure and certain physical properties of the graphite and boron nitride the latter is frequently called "white silica" or "white graphite" (in foreign sources this modification is often designated as s-BN). The β-BN has a cubic crystal lattice similar to the lattice of a diamond (Fig. 99), i.e., it is crystallized in the structure of zinc blende ZnS. The γ-BN has a hexagonal close-packed or tetragonal [628] lattice (frequently designated as R-BN). According to the most reliable data γ-BN is crystallized in a rhombohedral structure similar to the structure of β-graphite [733] with equal displacement between hexagons in consecutive layers [627]. This structure is shown on Fig. 98b. The lattice constants are: a = 2.504; c = 10.01 Å.

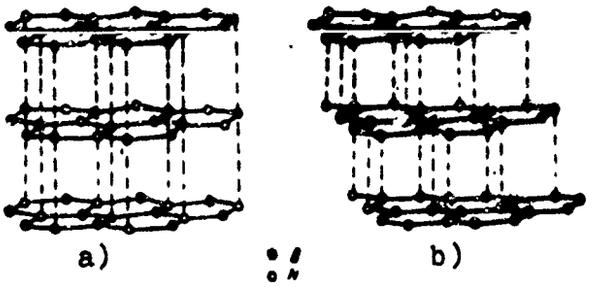

Fig. 98. Structure of hexagonal modifications of nitride of a boron: a) graphite-like; b) rhombohedral.

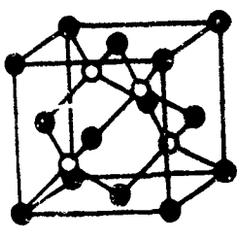

Fig. 99. Structure of the cubic modification of a boron nitride (borazon): ● – boron atoms; o – nitrogen atoms.

There are indications about the existence in the system boron-nitrogen of a nitride of the composition B_3N [629]; however, its existence is very problematical.

According to [1084], the hexagonal nitride of boron can have a disordered structure, which turns into normal with heating to a temperature above 2000°C. Defects of the packing of a hexagonal BN are examined in detail in [1013, 1085-1087].

Physical properties. Properties of a hexagonal boron nitride α-BN are studied most fully. The nature of the chemical bond in boron nitride has been studied in many works [631-633].

The distribution of the electron density in α-BN is similar to that in graphite (Fig. 100), where between the layers is 15-16% all electrons which corresponds to two electrons from every pair of atoms B-N in nitride (in graphite – one electron from each atom). Breger and Zhdanov [631] arrive at the conclusion concerning the

presence of the ionic bond between atoms of boron and nitrogen in the layers (approximate valence structure B^+N^-) and the absence of a metallic bond between the layers in contrast to graphite where the metallic bond is ensured by one electron. The presence of a boron nitride of a defined fraction of the ionic bond follows also from its position in the isoelectronic sequence LiF-BeO-BN-CC, where it is located between beryllium oxide, which has a clear ionic nature, and graphite with large fractions of covalence and metallic type of the bond.

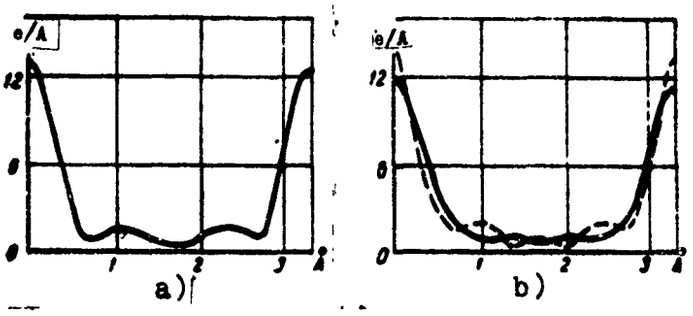

Fig. 100. Distribution of electron density in a crystal: a) boron nitride; b) graphite.

Pauling [1005] examined the structure and property of boron nitride from positions of the theory of resonance (resonance between $\rangle B-\ddot{N}\langle$ and $-B^- = N^+\langle$ is assumed).

Examining boron nitride from positions of concepts about the tendency of atoms in the formation of bonds to the stablest electron configurations, it is possible to consider that with the formation of the hexagonal boron nitride boron atoms chiefly transfer valence s^2p-electrons to nitrogen atoms, as a result of which boron atoms obtain a stable configuration s^2, and nitrogen atoms – s^2p^6. The presence of a defined (high statistical weight of s^2p^6-configurations of nitrogen atoms conditions, as is usual, the ionic fraction of the bond, and the energy isolation of these configurations conditions

the presence of the wide energy gap with subsequent dielectric properties of boron nitride (the interval between the filled and empty π-subband in BN is approximately 4.6 eV [674].

Dvorkin and his colleagues [634], on the basis of the heat of formation of the nitride determined by them, arrived at the conclusion of the presence of double bonds between the boron and nitrogen in links of layers of the structure.

According to data of [635], the distinction of energy of BN and graphite lattices is only 0.077 kcal/mole with the acceptance, as is made by Breger and Zhdanov, of one electron per atom.

Investigation of IR-spectrum of the absorption of boron nitride, conducted in [636, 637], showed the presence of two bands of intense absorption with wavelength of 7.28 and 12.3 μm (Fig. 101), which correspond, apparently, to two basic crystallographic directions with a sharply distinctive nature of the bonds.

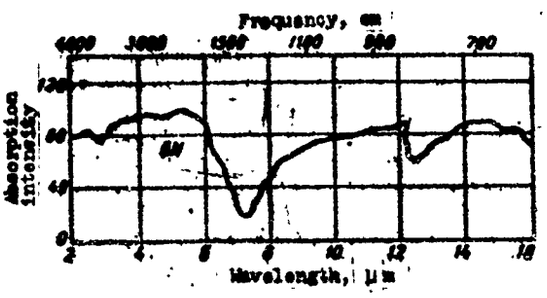

Fig. 101. Infrared absorption spectrum of boron nitride.

The distance between layers in the lattice of boron nitride equal to 3.34 Å is less than that for graphite (3.40 Å), which indicates the more durable bond between layers in the structure of boron nitride as compared to that of graphite.

The specific electrical resistance ρ of a hot-pressed sample of boron nitride decreases with temperature in the following way [638, 628]:

Temperature, °C	25	500	1000	1500	2000[1]
Specific electrical resistance, Ω·cm	$1.7 \cdot 10^{13}$	$2.3 \cdot 10^{10}$	$3.1 \cdot 10^{4}$	$2 \cdot 10^{3}$	$1 \cdot 10^{2}$

With an increase in density of articles of BN their resistance rapidly decreases, comprising for a porosity of 80% – 10^{12}, for 50% – $7 \cdot 10^{10}$ and for 10% – $5 \cdot 10^{9}$ Ω·cm.

These figures pertain to dry samples of nitride, and with moistening the electrical resistance rapidly descends, for example:

Relative humidity, %	20	50	90
Specific electrical resistance at 25°C, μΩ·cm	$7 \cdot 10^{12}$	$7 \cdot 10^{12}$	$5 \cdot 10^{9}$

The width of the forbidden band according to data given in [640] is 4.6 eV, which is characteristic for insulators. New measurements permit considering the width of the forbidden band to be narrower – from 3.6 to 3.8 eV.

The electrical resistance of the born nitride without structural defects, as was indicated is 10^{12} to 10^{13} Ω·cm, and with a decrease in the nitrogen content it is decreased, especially rapidly at 38-40 at. % of nitrogen (instead of those fixed by the formula of BN 50 at. %), there begins destruction of the base of the structure – plane lattices from atoms of boron and nitrogen.

With prolonged heating in a vacuum at high temperatures the electrical resistance of technical samples of boron nitride is stabilized, as one can see from data [641] given in Table 81. The samples were heated for a long time at a temperature of 500°C with subsequent heating at 1000, 1100 and 1400°C for 30 min, after which their electrical resistance was measured again at 500°C.

Table 81. Electrical resistance of boron nitride at a temperature of 500°C after preliminary heating in a vacuum.

Temperature of heat treatment in vacuum, °C	Resistance (Ω·cm) after heat treatment in a vacuum at 500°C		
	0 h	10 h	40 h
1000	$1,75 \cdot 10^{9}$	—	—
1100	$3,5 \cdot 10^{10}$	$4,2 \cdot 10^{12}$	$4,9 \cdot 10^{10}$
1400	$2,0 \cdot 10^{11}$	$2,0 \cdot 10^{11}$	$2,0 \cdot 10^{11}$

In work [1038] the electrical resistance is measured of samples of boron nitride and also of boron nitride with 2.5, 5 and 10% in the range of temperatures of 20-2000°C. A somewhat higher electrical resistance of boron nitride is set at room temperature, 10^{14} Ω·cm, as compared to earlier reduced data (10^{13} Ω·cm), and at 2000°C the electrical resistance is $2 \cdot 10^{2}$ Ω·cm. With an increase in the content of boric anhydride in boron nitride the resistance at first is increased somewhat (to $5 \cdot 10^{14}$ at 2.5% B_2O_3) and then (at 5-10% B_2O_3) decreases (to 10^{12} to 10^{13} Ω·cm). In the work the vacancy mechanism of conductivity is chiefly taken and it is shown that the activation energy of the intrinsic conductivity of boron nitride comprises 5.2 eV.

The dielectric constant and scattering factor (tg δ) of heated dry samples from boron nitride, measured [638] in the electrical field in parallel to the pressure applied with hot pressing of the samples (with the exception of a frequency of 10^{10} Hz, when the field was perpendicular to the pressure of hot pressing), are given in Table 82. Dielectric losses greatly depend on the humidity [641]. The dielectric strength (breakdown voltage) is 1.97-3.94 kV·mm [628].

The thermal conduction and coefficient of thermal expansion of boron nitride decrease with temperature (Tables 83 and 84 [638]).

Table 82. Frequency and temperature dependence of the dielectric constant and scattering factor of boron nitride.

Frequency, Hz	Dielectric constant			Scattering factor		
	10° C	330°C	500° C	10° C	330° C	470° C
10^3	4,15	4,4	9,0	0,00103	0,32	1,000
10^4	4,15	—	4,5	0,00042	0,0043	0,100
10^5	4,15	—	4,2	0,00020	0,0012	0,0058
10^6	4,15	—	—	0,00002	—	—
10^{10}	—	—	—	0,0003	0,004	0,0005

Table 83. Temperature dependence of thermal conduction of boron nitride.

Temperature, °C	Thermal conduction cal/cm·s·deg	
	In parallel to the direction of hot pressing	Perpendicular to the direction of hot pressing
300	0,036	0,069
500	0,034	0,067
700	0,032	0,065
900	0,030	0,053
1000	0,029	0,064

Table 84. Temperature dependence of the coefficient of thermal expansion of boron nitride.*

Temperature, °C	Coefficient of thermal expansion, x10-6	
	In parallel to the direction of hot pressing	Perpendicular to the direction of hot pressing
25—350	10,15	0,59
25—700	8,06	0,89
25—1000	7,51	0,77

*Coefficient of thermal expansion is measured for samples with a porosity of 4-5%.

On the average the coefficient of thermal expansion is about $2 \cdot 10^{-6}$ deg^{-1}. Nevertheless, the relatively high thermal conduction (perpendicular to the C-axis it is the highest among all the known dielectrics) and peculiarities of the structure condition the high stability of articles of BN opposite the thermal shock [638]. This pertains only to dry articles, whereas humid samples are destroyed already with thermal cycling of 20-600°C due to the mechanical effect of the evaporating moisture [641]. In a powdery state of boron nitride, especially produced by the reaction in the gas phase between BCl_3 and NH_3 with bulk density of approximately 0.1 g/cm^3 is, just as carbon black, a different heat insulator.

From calorimetric measurements [642] there results the following dependence of molar heat capacity of pure BN on temperature in the interval from 400° to 900°C

$$C_p = 5{,}030 + 12{,}6192 \cdot 10^{-3}(t - 22) - 6{,}5770 \cdot 10^{-6}(t - 22)^2.$$

Kelley for molar heat capacity in the interval from 0 to 900°C (accuracy ±5%) proposes another dependence

$$C_p = 7{,}61 + 4{,}00 \cdot 10^{-3}T.$$

The measurement of heat capacity of boron nitride at low temperatures carried out in [638] showed that within limits of temperature of 20-65°K the heat capacity obeys the law of the square of absolute temperature (and not the law of the cube, as it would correspond to the Debye law)

$$C_V = 14{,}4 \cdot \alpha RT^2/\theta,$$

where C_V – molar heat capacity.

This is explained by the laminar structure of nitride and the presence in it of quasi-two-dimensional lattices.

Table 85 gives values of enthalpies and heat capacity of BN according to [655], which are confirmed in work [775].

Table 85. Enthalpies and heat capacity of boron nitride [655].*

T, °K	$H_T - H_{298}$	C_p	T, °K	$H_T - H_{298}$	C_p
300	7,45	4,69	1000	5998,4	10,6
400	559,2	6,28	1100	6975,2	10,9
500	1252,2	7,50	1200	8084,4	11,2
600	2051,4	8,42	1300	9218,6	11,4
700	2929,4	9,09	1400	10371	11,6
800	3868,5	9,66	1500	11537	11,7
900	4860,5	10,2	1600	12708	11,7

*For composition B – 42.81, N – 56.85 ± ± 0.4%.

The characteristic temperature of boron nitride θ = 598°K.

Thermodynamic properties and behavior of boron nitride at high temperatures are most fully investigated in work [643]. Data obtained here are represented in Tables 86-89.

Table 86. Isobaric potential, of equilibrium constants and pressure of nitrogen of the reaction $BN_{TB} = B_{TB} + 1/2N_2$.

T, °K	ΔZ°, kcal	$-\lg K$	P_{N_2}, at.
1500	29,4	4,29	$2,52 \cdot 10^{-9}$
1600	27,2	3,72	$2,66 \cdot 10^{-8}$
1700	25,1	4,88	$1,06 \cdot 10^{-7}$
1800	23,1	2,81	$2,44 \cdot 10^{-6}$
1900	21,0	2,42	$1,48 \cdot 10^{-5}$
2000	19,2	2,11	$6,17 \cdot 10^{-5}$
2100	16,8	1,75	$3,11 \cdot 10^{-4}$
2200	14,7	1,47	$1,16 \cdot 10^{-3}$
2300	12,7	1,21	$3,76 \cdot 10^{-3}$

Table 87. Isobaric potential, of equilibrium constants and pressure of nitrogen of the reaction $BN_{тв} = B_{газ} + 1/2\ N_2$.*

T, °K	$\Delta Z'$, kcal	$-\lg K'_1$	P'_{N_2}, at.	$\Delta Z''$, kcal	$-\lg K'_2$	P''_{N_2}, at.
2500	23,2	2,03	$2,80 \cdot 10^{-2}$	62,2	5,54	—
2600	17,9	1,51	$6,25 \cdot 10^{-2}$	57,9	4,88	—
2700	12,5	1,01	$1,34 \cdot 10^{-1}$	52,5	4,25	—
280[illegible]	[illegible]	0,57	$2,67 \cdot 10^{-1}$	47,2	3,69	$2,22 \cdot 10^{-3}$
[illegible]	[illegible]	0,14	$5,12 \cdot 10^{-1}$	41,8	3,16	$4,97 \cdot 10^{-3}$
[illegible]	-3,4	—	>1	35,6	2,67	$1,05 \cdot 10^{-2}$

*$\Delta Z'$, K'_1 and P'_{N_2} — correspond to heat of reaction of 163 kcal.
$\Delta Z''$, K'_2 and P''_{N_2} — heat of reaction 203 kcal.

Table 88. Isobaric potential and pressure of sublimation of reaction $BN_{тв} = BN_{газ}$.

T, °K	$\Delta Z°$, kcal	P_{BN}, at.
2500	44,4	$1,14 \cdot 10^{-4}$
2600	40,0	$4,25 \cdot 10^{-4}$
2700	35,6	$1,21 \cdot 10^{-3}$
2800	31,3	$3,15 \cdot 10^{-3}$
2900	26,9	$9,12 \cdot 10^{-3}$
3000	22,6	$2,10 \cdot 10^{-2}$

Table 89. Isobaric potential, of equilibrium constants and pressure of boron nitride of reaction $B_{газ} + 1/2\ N_2 = BN_{газ}$.

T, °K	$\Delta Z°$, kcal	$K° \cdot 10^6$	P'_{N_2}, at.	P_{BN}, at.
2500	24,4	1,35	$2,80 \cdot 10^{-2}$	$1,3 \cdot 10^{-4}$
2600	22,2	1,32	$2,65 \cdot 10^{-2}$	$4,2 \cdot 10^{-4}$
2700	23,1	1,29	$1,34 \cdot 10^{-1}$	$1,3 \cdot 10^{-3}$
2800	24,3	1,26	$2,67 \cdot 10^{-1}$	$3,5 \cdot 10^{-3}$
2900	25,3	1,23	$5,12 \cdot 10^{-1}$	$8,8 \cdot 10^{-3}$
3000	26,3	1,20	>1	—

The temperature dependence of the elasticity of dissociation of boron nitride is expressed by equation

$$\lg p(\text{mm Hg}) = 4{,}0 - \frac{6450}{T}.$$

The heat of combustion of boron nitride $BN_{тв} + 3/4\ O_2 = 1/2\ B_2O_{3\ аморфн} + 1/2\ N_2$ is equal to 90.2 kcal/mole. At a heat of formation of B_2O_3 301.8 ± 1.4 kcal/mole, for the heat of formation of BN from elements a value of 60.7 kcal/mole is obtained [644], which sharply differs from the old data of Roth (33.5 kcal/mole) [645].

A similar value of the heat of formation is obtained calorimetrically and in [1020], and it is equal to 59.97 ± 0.37 kcal/mole.

The boron nitride is melted under the pressure of nitrogen (for suppression of dissociation) at a temperature of 3000°C [646].

The energy of dissociation of BN, according to [611], is within limits of 93-203 kcal/mole.

The spectrum of vapors of boron nitride gives two groups of lines: one from 4371.2 to 3772.7 Å and the other — from 3496.0 to 2180.0 [642].

The radiation factor of nitride of boron (monochromatic, when λ = 655 mμ) decreases within limits of temperatures of 800-1700°C from 0.64 to 0.62 [340].

Thermoemission properties of boron nitride were studied with the application of nitride powder on the binder on the tungsten core [170]. The saturation current at 2000°K is equal to 0.04 A.

An important property of boron nitride is the ability to be luminescent, which was noticed by Balmain. This ability was explained by many authors by the effect of impurities of boric anhydride and carbon and the presence in "amorphous" nitride of its crystal form. Remele [647] observed in 1911 effects of the action on a photographic film, ionization of air, formation of ozone, and the cause of fluorescence of the screen covered by barium cyanoplatinate. It was noted that such properties were possessed only by boron nitride prepared from borax and boric anhydride [648]. Similar works were conducted by Tiede and his colleagues [649-652]. Luminophor properties are possessed by a crystallized boron nitride (recrystallized through the melt of boric anhydride, borax, chloride, sulfate and sodium phosphate) [633]. In the work the following conclusions are made:

1) the activation of boron nitride by metals in contrast to usual crystalluminophors does not cause luminescence;

2) the best activator is carbon, which at low concentrations induces the blue and at high – yellow glow of the phosphor;

3) an increase in the content of boric anhydride in the BN-phosphor changes the color of the glow from blue to a pale green;

4) the nitride is activated well as a lumiiophor with excitation by light, ultraviolet rays and X-rays, α-particles and electrons (with excitation by light a very strong afterglow is revealed for 5 min, and with cathode excitation the afterglow very weak);

5) the glow is stably maintained with an increase in temperature up to 700-800°C.

A detailed investigation of luminescent properties of boron nitride, obtained by different methods and with different activators, is carried out in [1088]. In work [1089] the electroluminescence of a very pure boron nitride is investigated, and it is shown that the

dependence of the integral brightness on voltage can be represented by expression $B=B_0 \exp(-b/\sqrt{V})$.

Boron nitride, obtained at a temperature of 1200°C by the reaction of BCl_3 and NH_3 in a gas phase, is activated by the chlorine remaining in it [547]. It fluoresces in ultraviolet by a light-blue color and reveals a strong yellow-green phosphorescence.

As was noted in [654], the swelling and also cracking and destruction of articles from boron-containing materials with neutron irradiation connected with the burning out of isotope B^{10} are caused at first the accumulation and then the separation of helium, which formed with this nuclear reaction. In skelton crystal lattices helium atoms are stored to a considerable degree, which in the end causes disturbance of the lattices and in the case of layer lattices can pass between the latticed layers, and the effect of swelling can be reduced to a considerable degree. This pertains in the first place to boron nitride the effect on which irradiation by neutrons should be insignificant.

The mechanical properties of articles baked from hexagonal boron nitride by hot pressing are studied in detail in work [638]. The properties greatly depend on the direction of measurements — in parallel ($\parallel$) and perpendicular ($\perp$) to the direction of hot pressing, and the properties are essentially different. The tensile strength with compression for a sample with a density of 2.12 g/cm^3 (4-5% of the pores) is 32 and 24 kg/mm^2. The elastic modulus and tensile strength with a break sharply decrease with temperature, especially between 400 and 700°C (Table 90 and Fig. 102). However, with a further increase in temperature, as was revealed in investigation [1090], the strength of the boron nitride is again increased, reaching a maximum at 1500°C (Fig. 103). Boron nitride, hot pressed at low temperatures (900°C), which contains up to 14% boric anhydride, after heating in a vacuum at 1400°C reveals in the beginning a certain

increase in strength, and then the strength decreases with time [641]. According to the same data, the evaporation of boric anhydride from boron nitride in argon or nitrogen at 1800°C causes a lowering of the strength by 70%.

Table 90. Temperature dependence of strength and elastic modulus of boron nitride.

Temperature, °C	Tensile strength kg/mm²		Elastic modulus kg/mm²	
	Parallel extension	Perpendicular extension	Parallel extension	Perpendicular extension
25	11,12	5,10	8650	3440
350	10,60	4,90	6150	2430
700	2,70	1,33	1060	360
1000	1,53	0,76	1160	

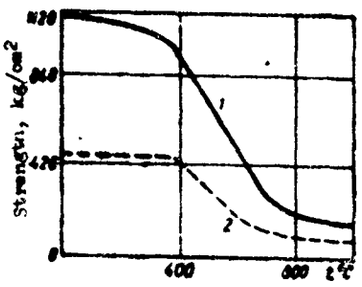

Fig. 102. Temperature dependence of tensile strength of boron nitride: 1 – in parallel to the direction pressing of the sample; 2 – perpendicular to the direction of pressing.

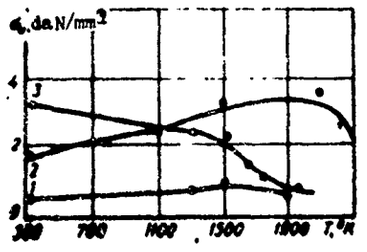

Fig. 103. Temperature dependence of tensile strength: 1 – boron nitride; 2 – material of the system B–Al–N; 3 – Si_3N_4.

The bending strength of boron nitride in practice is not changed up to 1900°K (at 1500°K an insignificant increase in strength is observed) [970].

The relatively high mechanical strength of articles from boron nitride permits treating them by cutting [636]. With the growth in them of the content of boric anhydride, the workability of them considerably worsens [641]. By machining it can be prepared from boron nitride complex articles — threaded bolts, nuts and so on (Fig. 104, according to [641]).

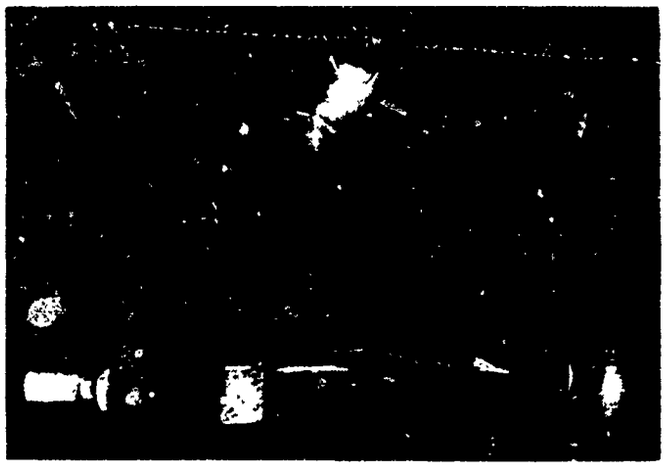

Fig. 104. Article of boron nitride.

The hardness of boron nitride is equal to 1-2 on the mineralogic scale [656]; however, it is changed substantially in the presence of boric anhydride and other impurities. The specific surface of the powder of boron nitride comprises 20,000-40,000 cm^2/g. The exceptional fineness of particles of the powder of boron nitride, together with peculiarities of its structure and low hardness, conditions its lubricating properties higher than that for graphite and molybdenum disulfide.

The friction factor of the freshly cut surface of boron nitride is 0.03-0.07, and with repeated wear it increases from 0.11-0.23.

According to [657], the friction factor increases at a temperature of 150°C up to 0.4 and at 600°C decreases down to 0.1, which is explained by the fusion of the impurity B_2O_3 and the appearance of liquid lubrication. At 900°C the magnitude of the friction factor considerably increases owing to the intense oxidation (see also [1091]).

Articles from boron nitride are resistant to abrasive wear. For example, the stability to the action of sand is equivalent to the stability to the action of glass.

The coarseness of particles of boron nitride considerably depends on the method of production. In work [658] dimensions of crystals were measured by the roentgenographic method: the width of the graphite-like layer L_a and thickness of the packet of parallel layers L_c of boron nitride obtained by different methods. The interlayer distance $d_{(002)}$ is measured also. Results of the measurements are given in Table 91 and are shown on Fig. 105. For boron nitride BN, obtained by means of gas phase reactions, $d_{(002)}$ is larger and L_a and L_c smaller than for that BN obtained by means of solid-gas phase or solid-solid-phase reactions. The crystallinity of BN is more noticeable with an increase in the temperature of the reaction and temperature of annealing of the formed nitride, where for BN, obtained according to the solid-solid-phase reaction, it is observed to a larger degree than for BN obtained according to the gas phase reaction.

Table 91. Dependence of dimensions of crystallites of boron nitride from the method and temperature of production [658].

Method of production	Temperature of reaction	$d_{(002)}$, Å	L_a, Å	L_c, Å
BCl_3+NH_3	900	3,619	45	12
	1050	3,591	49	18
Decomposition	800	3,624	56	14
$BCl_3 \cdot 4NH_3$	1000	3,594	66	14
$B_2O_3+NH_3$	800	3,389	71	45
	1000	3,339	290	65
$Na_2B_4O_7+NH_3$	300	3.319	265	85
	1000	3,339	1160	280
$B_2O_3+NaNH_2$	800	3,399	243	115

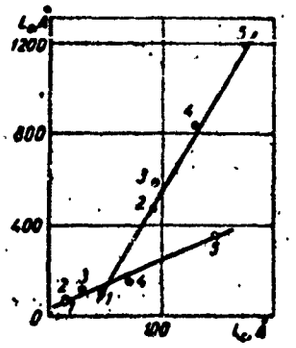

Fig. 105. Growth of crystals of boron nitride with heat treatment (annealing in a medium of nitrigen at 200 mm Hg): 1 – after synthesis; 2 – annealing at 1400°C; 3 – annealing at 1600°C; 4 – annealing at 1800°C; 5 – annealing at 2000°C; o – BN obtained by the reaction of BCl_3 and NH_3; ●–BN obtained by the reaction B_2O_3 and NH_3.

The powder of boron nitride usually consists of agglomerated particles. Such agglomerates have the form of either a circle with a diameter of ∿1 μm, or the form of stretched plates with transverse dimension of about 0.5 and length up to 20 μm.

The roentgenographic investigation of linear compressibility of boron nitride at pressures of up to 160,000 kgf/cm^2 [659] gave the following dependence:

$$\frac{\Delta C}{C} = 34 \cdot 10^{-7} p - 54 \cdot 10^{-12} p^2.$$

The compressibility of hexagonal boron nitride at higher pressures (up to 300 kbar) is investigated in work [992]. It was determined that the compressibility of boron nitride at all pressures is higher than that for graphite. At moderate pressures it is considerably more than that for diamond, and at high pressures it is considerably less than that for diamond.

Cubic boron nitride β-BN. Under high pressure the hexagonal boron nitride passes to cubic modification similar to the transition of hexagonal graphite into cubic diamond. Indications about the cubic modification of boron nitride have been available for a long time [660], [110]. Cubic boron nitride β-BN was produced by R. Uentorfom in a laboratory of the firm "General Electric" United States [661, 662, 663] and called "borazon." Crystals of cubic

boron nitride were produced at high pressures (45-75 kbar) and temperatures (1200-2000°C) from mixtures of the hexagonal nitride and nitrides of Li or Mg (as catalysts) with additions of certain impurities [664]. The addition of 0.01-1% Be in the form of a metal or salt causes the formation of crystals of cubic nitride of p-type, blue color, with an electrical resistance of 10^3 Ω·cm (in certain cases samples with ρ = 200 Ω·cm are produced). The activation energy of conductivity, determined from measurements of electrical resistance in the interval of temperatures of 25-400°C, comprises 0,19-0.23 eV. The type of conductivity was determined according to the sign of the thermoelectromotive force. It is assumed that beryllium replaces boron or nitrogen in the lattice of a cubic BN. The addition instead of beryllium of elementary sulfur leads to the formation borazon of the n-type, pale-yellow color, with an electrical resistance of 10^3-10^4 Ω·cm. Sulfur replaces nitrogen in borazon, which is indicated by the existence of the compound BS with cubic lattice, which forms at high temperature and pressure. The activation energy of conductivity of borazon of the n-type in the interval of temperatures of 25-250°C is 0.05 eV. With the addition to the initial mixture of compounds containing nitrogen and carbon, crystals β-BN will be formed with ρ = 10^5-10^7 Ω·cm and activation energy of conductivity of 0.28-0.41 eV. Sometimes β-BN with ρ = 10^6-10^9 Ω·cm will be formed directly from the initial mixture of nitrides of boron and lithium either of magnesium without any admixtures, possibly, due to the effect of the impurity of oxygen. The contact of p-BN with n-BN and p-BN with diamond (baked Al or ...) reveals the rectifying action. Measurements were conducted on a direct current of 10^{-6} A and voltage of 5 V.

The authors [1014] produced a p-type BN (from a mixture of 1 part by weight Be, 4 parts by weight of lithium nitride, 150 parts by weight of hexagonal boron nitride under a pressure of 58 kbar at 2000°C for 15 min). Its resistance proved to be equal to 1.10^{-6} to $5 \cdot 10^{-6}$ Ω·cm.

According to recently published results [1067], the specific surface energy of cubic boron nitride is equal to 4720 erg/cm^2 which yields only to the magnitude of surface energy of diamond (5378 erg/cm^2). According to the same data, the width of the forbidden band of borazon is equal to about 10 eV, i.e., pure borazon is a dielectric.

In work [665] by the method of the self-consistent field energy bands of cubic BN are calculated and it is shown that the energy of the gap between the bonds, which can be accepted as the width of the forbidden band, is equal to about 3 eV. The zonal structure of borazon is also investigated in [1093].

Geller [666] examined the bond B-N in hexagonal and cubic boron nitride. The distance of B-N in cubic BN (1.57 Å) is greater than that in the hexagonal (1.45 Å). A reduction of bond length leads to a greater change in energy than that for the C-C-bond. The binding energy in cubic BN is 4 kcal/mole and in the hexagonal 2-3 kcal/mole per 0.01 Å. The binding energy in cubic BN (35 kcal/mole) is lower than that in diamond (84.9 kcal/mole).

The electron circuit of the formation of borazon can be represented in the following way. Boron atoms, which have in an isolated state a configuration of valence electrons s^2p, as a result of s → p-transition acquire a sp^2-configuration, and then due to the attracting of a mobile electron of nitrogen atom — sp^3-configuration. Valence electrons of the nitrogen atom accomplish accordingly the following transformation: $s^2p^3 \rightarrow sp^4sp^3 + p$ and, transferring the p-electron to boron, obtain sp^3-configuration. Thus, in borazon there is created a high statistical weight of the atoms possessing sp^3-configurations of localized electrons, which ensures a cubic diamond-like structure of this bond. However, the statistical mobility of the p-electron of the atom of the nitrogen causes a certain lowering of the statistical weight of the sp^3-configurations of atoms of boron and nitrogen, which, in turn, conditions the smaller binding energy, the less high electrical resistance, smaller width of the

forbidden band and smaller hardness borazon as compared to diamond. On the other hand, the smaller part of rigid directional bonds in the lattice of borazon causes a somewhat greater degree of freedom with thermal exitation, in particular, a higher temperature of the polymorphous transformation in hexagonal nitride, which according to certain data consists even 2000°C [662], when for diamond it lies in the region of 900°C. For this reason borazon possesses greater thermal stability than does diamond and considerable more impact strength [667] as a result of the obtaining of the well-known "plasticity," induced by the appearance of a certain statistical portion of nonlocalized electrons.

The density of borazon is 3.45 g/cm^3, and the lattice constant a = 3.615 Å.

Physical properties of the rhombohedral modification of boron nitride γ-BN are practically not studied. Table 92 gives basic properties of boron nitride of three modifications (see also survey [1094]).

Table 92. Basic properties of modifications of boron nitride.

Characteristic	α-BN	β-BN	γ-BN
Content of boron, weight, %	43.6	43.6	43.6
Crystal structure	Hexagonal type of graphite	Cubic type of diamond	Rhombohedral type of β-graphite
Lattice constants Å:			
a	2,504 [626, 719]	3.615 [661-664]	2,504 [627]
c	6,661	-	10.01
c/a	2,662	-	4.0
Density, g/cm^3:			
X-ray	2.29 ± 0.0 [626]	3.45 [661-664]	∿1.80 [627]
pycnometric	2.20 ± 2.35 [648]	-	-
Bulk density, g/cm^3	0.1-0.7 [638]	-	-
Specific surface, cm^2/g	20,000-40,000 [638]	-	-
Heat of formation from elements, kcal/mole	60.7 [644]	-	-
Heat of combustion, kcal/mole	90.2 [644]	-	-

Table 92 Cont'd.

Characteristic	α-BN	β-BN	γ-BN
Melting point, °C (under pressure of nitrogen)	∿ 3000 [646]	-	-
Entropy, cal/mole·deg	20.77 [634]	-	-
Specific heat, cal/mole·deg	4.65 [655]	-	-
Thermal conduction, cal/cm·s·deg	0.036-0.059 [638]	-	-
Specific electrical resistance, Ω·cm	∿ 10^{13} [638]	10^3-10^4 [664]	-
Mohs hardness	1-2 [648]	∿ 10 [661-663]	-
Elastic limit with compression, kg/mm^2	24-32 [638]	-	-
Elastic limit with extension, kg/mm^2	5.11-11.12 [638]	-	-
Elastic modulus, kg/mm^2	3440-8650 [638]	-	-
Coefficient of thermal expansion $x10^{-6}$, deg^{-1}	0.5-1.7·10^{-6} [628]	-	-
Index of refraction	1.74 [638]	2.22 [664]	-
Double refraction	∿ 0.3	-	-

Chemical properties. In a chemical respect boron nitride is stable in a neutral and reducing gas media. Hydrogen and iodine do not act on nitride, and it reacts with chlorine with a red incandescence, forming trichloride boron. The chlorination of hot-pressed samples from boron nitride occurs very slowly at a temperature of 700°C and rapidly at 1000°C [638] (Table 93). By dry oxygen and CO_2 BN oxidizes rapidly at a temperature of 700-800°C with the formation of B_2O_3 + N_2. With the action of humid air, boiling water or diluted acids it hydrolyzes with the formation of ammonia and boric acid. The active oxidation of powder of boron nitride by humid air occurs at a temperature of 800-900°C, and with a two-hour heat treatment in air at 1000-1100°C the degree of its oxidation comprises 96-97% [668]. The oxidizability of nitride powder substantially depends on the temperature of its preliminary heat treatment ("stablization"). Thus with an increase in temperature of the preliminary heat treatment in a nitrogen-containing medium from 1000 to 1600°C the rate of its oxidation decreases four times [639].

Table 93. Decrease of weight with chlorination of boron nitride, mg/cm^2.

Time, h	700°C	1000°C
3	—	2,7
20	0,25	17,0
40	0,55	—

Increased especially sharply is the resistance of boron nitride to oxidation with its preliminary heat treatment in nitrogen at temperatures of 2200-2400°C; at these temperatures the specific surface of the nitride powder is greatly reduced, and its resistance to oxidation approaches resistance of compact boron nitride obtained by hot pressing [1030]. Oxidation of nitride powder starts at 770°C and occurs slower the more the nitride powder is contaminated by boric anhydride. At higher temperatures volatilization of B_2O_3 predominates, and the powder is oxidized at a high rate. Hot-pressed, quite dense samples of boron nitride (porosity of 4-5%) oxidized the air weakly. The decrease in weight of the samples with oxidation, according to data of [638], is given in Table 94.

Table 94. Decrease in weight with oxidation of boron nitride in air, mg/cm^2.

Time, h	700°C	1000°C
2	0,014	0,35
10	0,062	0,85
30	0,138	4,8
60	0,235	10,0

With carbon the boron nitride reacts at temperatures above 2000°C with the formation of boron carbide and nitrogen carbide [669], and with the reaction with refractory metals or their carbides at high temperatures corresponding borides will be formed [670, 671]. The resistance of boron nitride in the form of hot-pressed

samples in different corrosion media at room temperature in the course of seven days is investigated in [638], and the obtained results are given in Table 95. Samples of stabilized boron nitride sufficiently are stable at a temperature of 190-300°C in HCl, H_2SO_4, H_3PO_4 (pure and with additions of oxidizers – $KMnO_4$, $K_2Cr_2O_7$, $KClO_4$). The most rapidly decomposed is 5% H_2SO_4, and the best activator of the decomposition is $KClO_4$.

Table 95. Corrosion resistance of boron nitride.

Corrosion medium	Decrease in weight mg/cm^2	Decrease in tensile strength of samples* with extension
H_2SO_4 (concen.)	None	None
H_2SO_4 (20% concen.)	10.7	60
H_3PO_4 (concen.)	1.3	23
HF (concen.)	17.5	55
HNO_3 (concen.)	8.9	70
NaOH (20% concen.)	8.9	82
CCl_4	1.3	20
Gasoline	1.6	None
Benzine	0.4	None
Ethyl alcohol (95% concen.)	14.6	48
Acetone	13.0	32

*The initial value σ was 5.18 kg/mm^2.

In the chemical analysis of boron nitride for the content of nitrogen (according to K'dal [Translator's note: name not verified]) it is usually decomposed by boiling concentrated H_2SO_4 with an addition

of K_2SO_4. Methods of chemical analyses of boron nitride are given in [276, 673].

Fluoric acid strongly acts on boron nitride. Hot alkalis decompose it with the separation of ammonia [574]

$$3BN + 3H_2O + 3OH^- \rightarrow (BO_3)_3 + 3NH_3$$

Boron nitride is not moistened by melted glass at 750°C in air; lead glaze, which melts at 850-900°C, moistens the nitride in air but does not moisten it in an inert gaseous environment; the nitride is moistened by boron phosphate at 1400°C in nitrogen. Silicon, aluminum, bronzes do not moisten the nitride [641]. The last one also almost does not interact with the melt of cryolite.

The hexagonal boron nitride adsorbs argon just as graphite, and the distinction in heats of adsorption of argon by these substances is small (2.2 kcal/mole for the nitride; 2.3 kcal/mole for graphite), and in this case the adsorbed argon film is nonlocalized [675].

In the reaction with gas flows having high speeds, at temperatures of 6000-7000°K and atmospheric pressure [676] the boron nitride rapidly erodes in air (0.117 ft/s·inch^2) and slower in a rocket exhaust gas (0.061), and also in nitrogen (0.026). An analysis of the obtained data shows that increased erosion in air flows only in a small degree can be attributed to oxidation and basically is caused by processes of mass and heat transfer, the portion of which pertains to 76% of the erosional removal of nitride (see also [1092]).

Boron nitride is very stable in lithium vapors at a temperature of 2000-2500°C and pressure 0.1-1 mm Hg, substantially exceeding in this respect all other fireproof materials, especially oxides of aluminum and zirconium and also zircon [677].

High stability reveals the boron nitride with respect to the effect of slags formed with the smelting of ferromanganese, manganese and silicomanganese, not being destroyed at temperatures of 1600-2000°C for 10-15 h [678].

Methods of producing boron nitride. Many methods of producing hexagonal boron nitride are known, and they can be classified in the following way.

1. Heating of boric anhydride, boric acid or borax with cyanogen sodium, potassium or calcium [625, 679] with amides [717]

$$B_2O_3 + 2NaCN = 2BN + Na_2O + 2CO.$$

The reaction was carried out with the use of calcium cyanide at a temperature of 1200°C [630], sodium cyanide at 2000°C [680], hydrogen cyanide with boron at 750°C [681], and by the action of urea on boric anhydride [682]. All these methods are complicated, require high pressures and temperatures and give as a result contaminated nitride.

A method somewhat better described in a patent [717] of producing boron nitride by means of reaction of boric anhydride or boric acid or its alkali salts with the amide of alkaline metal in the interval of temperatures 210-1000°C (in most cases at 300-500°C). Of the amides the most expedient to use is the sodium amide $NaNH_2$, and of the boron-containing compound – borax or boric anhydride

$$B_2O_3 + 3NaNH_2 = 2BN + NH_3 + 3NaOH,$$
$$Na_2B_4O_7 + 5NaNH_2 = 4BN + NH_3 + 7NaOH.$$

The process is carried out in a melt, in a medium of ammonia, with a surplus of amide. The product of the reaction is treated

with water for the removal of impurities and then stabilized with heating at a temperature of 1800-2200°C for 2 hours. Here the nitride becomes resistant to the action of acids and alkalis. The yield of boron nitride by this method is 60-70%, which considerably exceeds the yield in the use of the reaction with potassium cyanide, where it comprises 22%.

2. Treatment of boric anhydride and boric acid or its salts by chlorous ammonium [652, 683-685]

$$B_2O_3 + 2NH_4Cl = 2BN + 2HCl + 3H_2O.$$

and also by chlorous ammonium with additions of magnesium [686]. In the last case two parts of boric anhydride heat in a mixture with one part of magnesium and three parts NH_4Cl at a temperature of 300°C. Tiede and Tomaschek [652] carried out this method with the use of borax, a mixture of which with NH_4Cl in a molecular ratio of 1:2 is heated

$$2NH_4Cl + Na_2B_4O_7 = 2NaCl + H_2O + 2NH_3 + 2B_2O_3,$$
$$B_2O_3 + 2NH_3 \rightarrow 2BN + 3H_2O.$$

The produced product is washed with water and dried.

3. According to Mayer and Zappner [687], boron nitride is produced by the transmission of current of boron chloride in a mixture with hydrogen with a surplus of ammonia through a quartz tube heated to 600°C. Then the temperature gradually rises approximately up to the temperature of 1000°C, at which the reaction

$$4NH_3 + BCl_3 = BN + 3NH_4Cl.$$

occurs.

This product is heated at 1000°C in a current of nitrogen. The content of nitrogen in the thus produced product consists 55.68% (as compared to 56.02% from the calculation for BN), and the content of BN in the product is 99.44%.

Later this method was patented [705] in the following form. Boron carbide is subjected to chlorination with the formation of trichloride boron: $B_4C + 6Cl_2 = 4BCl_3 + C$. Then BCl_3 is treated by ammonia: $BCl_3 + 4NH_3 = BN + 3NH_4Cl$. The first stage is carried out by the passage of chlorine above boron carbide heated to 500°C, and the second – with heating of the mixture with ammonia at first at 500-1000°C, and then to 1600-2200°C (optimum temperature is 1800°C). The finished product is stabilized by heating at 1000-2000°C.

A similar method of the formation of boron nitride is used in [574], where BN was produced by passage of the mixture $N_2 + BCl_3$ through the internal nozzle of a quartz "injector" and ammonia – through the external nozzle. A reaction occurred at a temperature of 800-1500°C, and the layer of nitride was deposited on the graphite plate located above injector. It is indicated that instead of ammonia it is possible to use phosphorus nitride chloride ($NPCl_2$) and other similar compounds.

In a patent [706] the method of producing boron nitride is described by the reaction in a gas phase between ethylborate (or methylborate) and ammonia at a temperature of 850-900°C with subsequent treatment of the produced product by ammonia at higher temperatures (950-1100°C). The yield of boron nitride in this case consists up to 96%, the content of boron, up to 42.9 and nitrogen, up to 54.4%.

The second variant of methods founded on the use of boron halides consists in the reaction of bromide boron with liquid ammonia [689], as a result of which a mixture of bromide ammonia,

$Br(NH_2)_3$ and $Br(NH)_3$ will be formed. After the evaporation of the surplus of ammonia, the mixture is heated at 750°C in a current of ammonia, obtaining in the dry residue of boron nitride. Similar to this method is also the method of Stock and Blix [691], which consist in the decomposition of B_2NH_3, which at a temperature of 125°C quantitatively decomposes into BN and ammonia. The yield here is small, but the nitride produced is very pure.

4. Treatment of boric anhydride by ammonia [692, 693], nitrogen or ammonia in the presence of carbon as a reducer [639, 694-698]

$$B_2O_3 + 2NH_3 = 2BN + 3H_2O.$$

With the heat treatment of boric acid in a mixture with carbon, in the current of nitrogen at a temperature of 1000-1100°C the yield of boron nitride does not exceed 3-4% even at great pressures of the nitrogen up to 7 at, [696], which is connected with the formation on the surface of particles of boric anhydride in the current of ammonia of a very thin and dense film of nitride, which prevents the flow of the reaction [685]. The thickness of this film, according to data of Podszus [639], with heating for 100 hours of boric anhydride in a current of ammonia at a temperature of 1100°C, consists 10-20 μm.

For the production of boron nitride the authors [694] heated a mixture of 12 parts by weight of boric anhydride with 11 parts by weight of carbon in a current of nitrogen. At atmospheric pressure and a temperature of about 1700°C the maximum yield consists of 26.6%. In carrying out of the reaction under the pressure of nitrogen of 70 at and at a temperature of 1600°C, yield is increased up to 85.8%.

To increase the gas-permeable charge and reactionary surface, besides the crushing of powder of the initial boric anhydride, it

is proposed to boric anhydride on linings serving to increase the interface of the phases and also to introduce into the charge substances separating with heating volatile components. Thus, in work [696] it is reported that with the preliminary heat treatment of 1 part by weight of boric acid with 2 parts by weight of calcium phosphate and the subsequent heating of the mixture in a current of nitrogen in a graphite tubular furnace of a mixture of 2.5 parts by weight of calcium borate and 1 part by weight of carbon at 1400°C.

Two variants of such a method of producing boron nitride are known [697]. One of them is calculated for the creation of a sponge of boric anhydride with a very porous and fine structure and consists in heating up to 1200°C a mixture of 1 part by weight of boric acid and 3 parts by weight of NH_4Cl with the passage of ammonia with a rate of 1 $l/h \cdot cm^2$.

Another variant assumes the use of charges with linings of such compositions (by weight):

$$32\%\,H_3BO_3 + 30\%\,Ca_3(PO_4)_2 + 38\%\,NH_4Cl,$$
$$40\%\,H_3BO_3 + 20\%\,CaCO_3 + 40\%\,NH_4Cl,$$
$$45\%\,H_3BO_3 + 15\%\,MgCO_3 + 40\%\,NH_4Cl.$$

The process of nitration is conducted, just as in the first case, for 24-40 hours with subsequent washing of nitride powder by acids.

In patents [699, 707] it is recommended to use calcium phosphate as the lining, mixing it with boric anhydride in an equimolar ratio with heating of the mixture in a medium of ammonia at 800-1000°C (optimum temperature is 900°C).

The same recommendations are given in patent [708], but as a lining calcium phosphate alone is not used but its mixture with

boron nitride. The product of nitration of the mixture of such a lining with boric anhydride at 900°C is treated at first by acids for the washing of impurities and boric anhydride, and then it is stabilized by heating at temperatures of the order of 1200-1500°C (the duration at 1200°C consists 40-60 hours, at 1300°C, 5-16 hours, at 1400°C 1-5 hours, at 1500°C, 0.5-1 hour). The content of BN in such a product is 95%, the density is 1.9 g/cm^3, the maximum dimension of particles of stabilized boron nitride is 1.5 μm, and average dimension is about 0.3 μm.

A similar kind of technological processes are recommended for production [641].

As the lining, which consists of up to 70% of the weight of the charge, Podszus [639] used boron nitride, and nitriding was carried out in the furnace shown on Fig. 106 at a temperature of 1000°C. Two carbon electrodes 1 (8 × 8 cm) with copper busbars 2 ensure current feed to the reaction mixture 3. Placed between electrodes is a thin carbon rod 9, which plays the role of a heater at the beginning of the process. For thermal insulation the furnace is lined with boron nitride 4, zircon 5 and fire clay brick 6, and further an iron housing 7 with approximate fittings follows. Ammonia is fed through the pipe 8. Furthermore, he developed a furnace for the continuous process of production nitride, founded on the counter movement through the pipe of the furnace of boric anhydride and current of ammonia. The productivity of such a furnace with a diameter of 60 mm consists 0.6 kg of nitride in 1 hour.

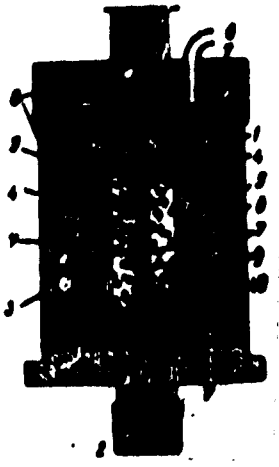

Fig. 106. Furnace for the production of boron nitride (according to Podszus).

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The profitableness of the use of boron nitride as a lining is confirmed also by Moskvin [653].

Boron nitride can be obtained from a "sponge" (B_2O_3 + C) formed by the dehydration of boric acid in a mixture with carbon [638]. The sponge is placed in a boat of boron nitride and treated with ammonia. It was determined that it is most convenient to obtain boron nitride by means of treatment of the charge B_2O_3 + NH_4Cl by ammonia at a temperature of 1100-1200° [700, 701]. The charge is prepared on the base the sinter B_2O_3 + CaO, produced by means of heating of the mixture of boric acid with chalk, during which there occurs the dehydration of boric acid and decomposition of $CaCO_3$ with the formation of a very thin distribution of boric anhydride over CaO particles and with the partial formation of calcium borate (Fig. 107). With the ratio of components in the mixture (in moles) H_3BO_3:NH_4Cl:$CaSO_3$ = 1:1:0.25 boron nitride produced, almost exactly corresponding to formula BN, with the sum of the content of boron and nitrogen close to 100%, and the yield reaches 92-93% instead of 70-80% according to earlier proposed similar methods. It is necessary to note that in such a way the most fine-grained powder of boron nitride will be formed.

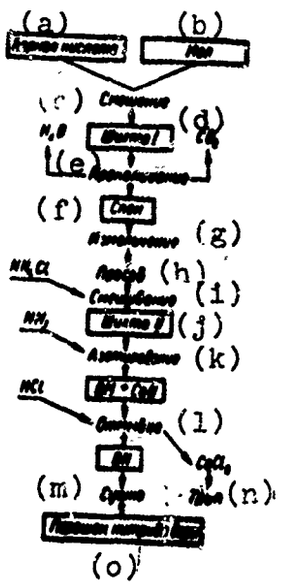

Fig. 107. Flow diagram of production of nitride of boron.
KEY: (a) Boric acid, (b) Chalk, (c) Mixing, (d) Charge I, (e) Calcination, (f) Sinter, (g) Crushing, (h) Sifting, (i) Mixing, (j) Charge II, (k) Nitriding, (l) Washing, (m) Drying, (n) Trap, (o) Powder of boron nitride.

This group of methods of production of boron nitrides includes heating in a current of nitrogen of borate calcium in a mixture with carbon [648]

$$CaB_4O_7 + 8C + 3N_2 = 4BN + Ca(CN)_2 + 7CO.$$

For producing boron nitride for luminophors, heat treatment of borax with chlorous ammonium is also used [702].

Authors [703] investigated in detail the process of nitration B_2O_3 in a mixture with carbon described by the total reaction

$$B_2O_3 + 3C + N_2 = 2BN + 3CO.$$

In this case, just as in [638], a "sponge," produced by dehydration of the mixture of boric acid with carbon black was used.

For nitration the sinter by portions of 200-300 g each were loaded in graphite boats, which were placed in the electric furnace of resistance with a graphite tubular heater (Tamm furnace), into which current of nitrogen purified of oxygen and moisture was fed.

Results of a preliminary investigation showed that from a charge of stoichiometrical composition of 71 wt. % of H_3BO_3 and 29 wt. % carbon black a product is produced which is greatly contaminated by carbon, and therefore further experiments were conducted with charges containing a smaller quantity of carbon black – 25, 20, 15 and 10 wt. % as compared to 29% with respect to stoichiometry. It was assumed that a balance will be reached between the boric anhydride remaining in the charge after partial volatilization and the decreased content of carbon black in the charge, and partly the deficiency of carbon in the charges will be replenished due to graphite of the boat and pipe of the furnace by means of transfer through the gas phase containing carbon monoxide. Mixing and

dehydration were conducted just as it was above, however, the time of pulverizing the sinter produced from a charge with 10% carbon black consisted of 8-10 hours. As follows from Figs. 108 and 109, starting from the temperature of nitration of 1600°C, in most cases the sum of the content of boron, carbon and nitrogen in nitration products is close to 100%, which indicates the termination of the process of reduction of the boric anhydride.

The maximum content of nitrogen in products of nitration is reached at 10% carbon black in the charge, evenly descending at 15 and 20% and sharply at 25% carbon black in the initial charge. The yield of boron nitride, on the contrary, is increased with an increase in the content of carbon black in the charge. Products produced with large contents of carbon black consist of a mixture of carbide and nitride of boron, which indicates the preferential formation of boron carbide.

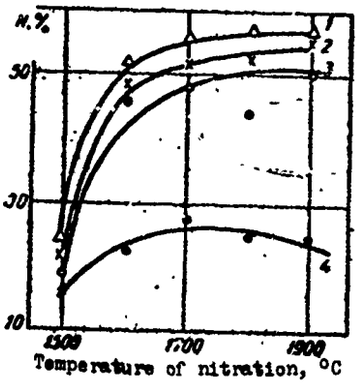

Fig. 108. Dependence of the content of nitrogen in nitration products of sinters of boric anhydride with carbon black on the temperature and content of the carbon black in the initial charge: 1 – 10; 2 – 15; 3 – 20; 4 – 25 wt. % of carbon black.

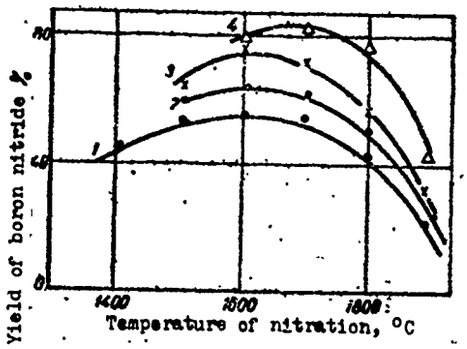

Fig. 109. Dependence of the yield of boron nitride on the content of carbon black in the initial charge and the temperature of nitration: 1 – 10; 2 – 15; 3 – 20; 4 – 25 wt. % of carbon black.

The mechanism of reduction and nitration on the basis of the obtained data can be described in the following way. The above reaction of the process is a total one and consists of reactions of reduction of boric anhydride with carbon to the boron and the carburization or nitration of the latter. At small contents of carbon in the initial charge all of it is expended for the reduction of boric anhydride, and the boron produced is nitrated to the nitride, and the surplus of boric anhydride volatilizes, which causes the small yield. With an increase in the content of carbon black in the charge the quantity of reduced boric anhydride is increased, and the degree of nitration of it, other things being equal, decreases and the yield increases. With 25% content of carbon black in the charge the forming reduced boron combines with the carbon into carbide, and together with this part of the boron is nitrated with the formation of nitride. From Fig. 109 it is clear that the maximum yield of boron nitride in all cases is attained at 1600-1700°C when the high volatility of boric anhydride is suppressed by reactions of reduction and nitration. At higher temperatures preferential value is given to the high volatility of the boric anhydride, and the same is observed and at lower temperatures insufficient for the development of reactions of reduction and nitration, as was shown in [714].

Optimum conditions of the production of boron nitride are the following: the use of charges, with the nitration of which there occurs most fully the process of reduction of boric anhydride, but there does not remain a surplus of carbon capable of combining with boron into a carbide; temperatures at which process of the reduction and nitration prevail over the process of the evaporation of boric anhydride; the time of nitration, sufficient for the nitration of the formed boron. Proceeding from results obtained, for three-hour nitration, the optimum conditions are the temperature of 1700°C, and the most favorable content of carbon black in the initial charge — 15%. It was determined that the yield of nitride and content of nitrogen in it can still be increased with use of two-phase nitration

at temperatures of 1500 and 1700°C. The chemical composition of such nitride is 43.1-43.4% B, 55.2-55.9% N and up to 0.1% C.

Consequently, unsatisfactory results of experiments of Stähler and El'bert [694] should be cited due to the use by them of not sinters but mixtures of boric anhydride with carbon, which possess small reaction surface. For confirmation of this in the work experiments with charges produced by mechanical mixing are conducted. It is revealed that the yield of boron nitride does not exceed 3-4%, and nitration products are greatly contaminated by the carbon.

Thus, it is shown that the content of carbon black in the charge and also the reduction temperature (nitration) can be selected on calculation for the maximum suppression of high volatility of boric anhydride. At 15 wt. % of the carbon black in the charge H_3BO_3 + C and at the temperature of nitration of 1700°C there is attained a composition of boron nitride close to stoichiometrical, with a yield of 60-70% as compared to a yield in 26% and low quality of the nitride, which was obtained in preceding works by the nitration of mechanical mixtures of boric anhydride with carbon.

A similar method is exploited in the USSR in large scales of the industrial production of boron nitride for the subsequent manufacture of fireproof articles.

5. Direct nitration of boron. Further Moissan [709] proposed to obtain boron nitride by the action on boron of nitrous oxide, in work [710] the direct nitration of amorphous boron in a stream of nitrogen is described. The product obtained at a temperature of 1600°C contained 94.3% BN, and an increase in temperature up to 2000°C increases the yield to 99.5%.

The temperature dependence of the constant of nitration of boron powder (Fig. 110) is changed sharply with transition from 1200 to 1300°C [704]. Since the roentgenographic investigation does

not reveal here any structural changes and the appearance of new phases, then one should consider that the retardation of diffusion at temperatures above 1200°C and the simultaneous decrease in activation energy occur due to correction of the lattice, which leads to the completion of the already formed plane layers from boron atoms, not all free nodes of which are filled by nitrogen atoms. Thus, there occurs filling of nodes of the already constructed base of the lattice, which requires less energy than that for the organization of the actual lattice; however, the process of filling occurs relatively slowly due to the "search" by nitrogen atoms of vacant places. From equations of the temperature dependence of the coefficient of reaction diffusion of nitrogen into boron

$$D_{600-1200^\circ C} = 30100 \exp(-30650/T),$$
$$D_{1300-1500^\circ C} = 20{,}3 \cdot 10^{-5} \exp(-2000/T)$$

it is clear that the activation energy with transition from a temperature of 1200 to 1300°C decreases from 61.3 to 4 kcal/mole. The last quantity is close to the energy of the cohesion between layers of atoms in the lattice of graphite equal to 4.36 kcal/mole, i.e., the migration of nitrogen atoms occurs not in plate lattices of defective structure of the nitride but between them. The magnitude of 4 kcal/mole is close to the magnitude of binding energy between plane lattices in the structure of nitride.

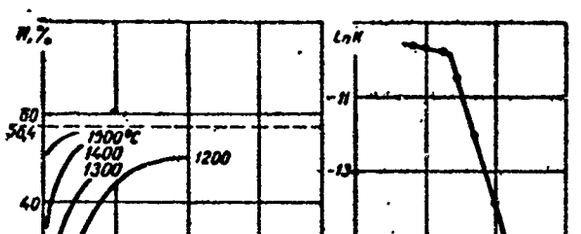

Fig. 110. Nitration of boron: a) isotherms of nitration; b) temperature dependence of the logarithm of the nitration constant.

The method of production of boron nitride by direct nitration of boron is expensive and cannot be used in industry [641].

Above mention was made about the formation of the cubic modification of boron nitride – borazon, which occurs similar to the formation of artificial diamond – under high pressures and at high temperatures with the use as catalysts of additions of alkali and alkali earth metals (according to [663] – under pressure of 62,000 at. and at a temperature of above 1350°C).

Without catalysts cubic crystals of boron nitride will not be formed even under pressures of 100,000 at. and at temperatures of more than 2000°C. Wentorff [664] showed that additions of transition metals do not promote the formation of Borazon. Positive results are given by additions of alkali, alkali earth metals, antimony, tin, and lead. It is noted that pressure and temperatures necessary for allotropic transformation increase with an increase in atomic weight of the addition. It can be assumed that the "catalytic" action of the indicated additions is included in the transfer of electrons to boron atoms with increased statistical weight of sp^3-configurations necessary in turn for the formation of borazon. Therefore, good catalyzers are alkali and alkali earth metals, which easily give their valence electrons for the stabilization of sp^3-configurations, and also tin and lead, which, besides the ability to transfer quite easily nonlocalized electrons, have themselves the known statistical weight of sp^3-configurations formed by localized fractions of valence electrons. In the same way antimony is the source of sp^3-configuration and mobile electrons formed according to diagram $s^2p^3 \rightarrow sp^4 \rightarrow sp^3 + p$. Bismuth following it must not possess such properties, since part of its valence electrons passes to the vacant f-shell. According to the same considerations the effectiveness of "catalysts" decreases with an increase in atomic weight of the addition. For alkali metals and also alkali earth metals with the formal increase in atomic weight, transitions of

valence electron to the vacant d-state with the stability of configuration of electrons on these states increasing with the growth in the main quantum number. The latter leads to a decrease in the possibility of the transfer of valence electrons for an increase in statistical weight of sp^3-configurations of boron atoms into boron nitride. Connected with these circumstances is the "catalytical" action of nitrides of the above metals. In the formation of nitrides, for example, alkali metals, the probability is increased of the transition of valence electrons of atoms of these metals to the nitrogen atom, which prevents transitions of electrons to the d-states and the formation by them of stable configurations which are difficult to disturb. On the other hand, only part of these electrons will form with nitrogen of the s^2p^6-configuration, they are weakly attached both to atoms of the metal and nitrogen, and they can participate in the formation of sp^3-configurations by boron atoms. The role of these nitrides as media through which recrystallization occurs of hexagonal nitride into cubic is either doubtful or plays a secondary role [614]. For the mechanism of the action of catalysts see also [1095-1098].

The original method of producing borazon is described by Vickery [718], which consists in the substitution of phosphorus by nitrogen in boron phosphide BP having a diamond-like structure.

$$BP + NH_3 \rightarrow BN + PH_3.$$

The authors [817] propose to obtain a cubic boron nitride by the reaction of boranes or boron chlorides with ammonia, nitrogen or a mixture of nitrogen with other gases, for example, hydrogen, with the introduction into zone of reaction of primings having cubic structure (α-Fe, zinc blende) in the form of the finest particles of an aerosol.

The rhombohedral modification of boron nitride is produced by the reaction of $NaBO_2$ with NH_4Cl at a temperature of 1000°C, borax

with potassium cyanide, and also by the decomposition trichlorborazole at 900°C [627]. Rhombohedral nitride is not obtained in pure form, but will be formed in mixtures with hexagonal nitride.

Producing of articles and materials from boron nitride. Articles from boron nitride are produced either by sintering of billets preliminarily pressed by different methods or by hot pressing. In the first case hydrostatic pressing is used in elastic forms under a pressure of 7 t/cm^2 with subsequent sintering in a medium of nitrogen or dry ammonia [669]. A favorable effect is noted on the process of sintering of additions to nitride powder of volatile impurities, especially B_2O_3. According to [641], billets from powder of boron nitride are pressed with the use of water as a binder added in small quantities. After drying at a temperature of 110°C the billets are baked in a medium of ammonia at 1800°C or a medium of nitrogen at higher temperatures. Simultaneously with sintering purification of the boron nitride from volatile impurities occurs.

For the pressing of the billets in metallic molds pressures of 0.7-2 t/cm^2 are recommended with subsequent sintering at a temperature of ~1400°C. The density of articles with this method is small and consists 1.1-1.2 g/cm^3, and shrinkage in the process of sintering is not observed.

For the production of dense articles from boron nitride, hot pressing is used. Thus, in [638] by hot pressing samples of boron nitride with a density of up to 2.1 g/cm^3, i.e., with a porosity of 5-7% are formed. It is recommended to conduct hot pressing in graphite molds at 1500-1900°C under a pressure of not less than 16 kg/cm^2 [699, 707], or at 1700-1900°C under a pressure of 140 kg/cm^2 [708].

The pressure of pressing substantially affects the density of hot-pressed articles from boron nitride. Thus, articles from boron nitride with relatively high density (94%) are produced by hot pressing under a pressure of 600 kg/cm^2 at a temperature of 1900°C [974].

An investigation of BN hot pressing, carried out in works [975-1099], showed that baked the most actively with hot pressing is powder of boron nitride, synthesized at low temperatures (from the charge H_3BO_3 + $Ca_3(PO_4)_2$ in a current of ammonia at 900-1000°C. The high dispersity of this powder and imperfection of the structure conditions its recrystallization and active sintering. According to these data, optimum conditions of hot pressing are: temperature of 1800°C and pressure of 300 kg/cm^2. Samples produced according to these conditions have a density of 2.06-2.08 g/cm^3, i.e., porosity of the order of 0.1%. With sintering particles of boron nitride are sharply enlarged from 0.06-0.2 μm in the powder of low temperature nitride to 60-80 μm in a hot-pressed sample.

The authors [641] studied the effect of the additions of boric anhydride to boron nitride with hot pressing at 1700-1900°C and pressures of 100-200 kg/cm^2. The addition of boric anhydride permits increasing the density of the articles up to 2.6 g/cm^3, but the chemical stability of the produced articles greatly decreases. For the producing of dense technical articles on the base of boron nitride, in this work additions of calcium aluminosilicate (5-10%), of boron phosphate BPO_4 (10%), and also aluminum (to 5%) and of aluminum nitride (1-5%).

A new form of technical materials from boron nitride is boron pyronitride, which, represents crystal-oriented formations similar to pyrographite. The structure and properties of pyrolytic boron nitride are described in [711-714]. The producing of pyrolytic nitride is similar to the producing of pyrographite [715-716] and consists in the reaction of volatile compounds of boron and nitrogen according to definite technological conditions.

The boron pyronitride is deposited on a hot base layer in the form of dense fine-grained substance, transparent in small pieces and semitransparent in layers with the thickness of about 0.5 mm. The structure of the material represents columnar cones characteristic

for pyrographite. However, as is noted in [712], the preferable orientation of boron pyronitride is expressed much weaker than that of pyrographite.

Properties of pyrolytic boron nitride essentially depend on the direction – parallel (a) or perpendicular (c) to the surface of deposition.

Table 96 gives certain properties of pyrolytic boron nitride.

Table 96. Properties of pyrolytic boron nitride.

Characteristic	Parallel to the surface of deposition (a – direction)	Perpendicular to the surface of deposition (c – direction)
Crystal structure	Hexagonal type of graphite	
Coefficient of thermal expansion, deg^{-1}:		
20°C	$-2.9 \cdot 10^{-6}$	-
700°C	0	$40.5 \cdot 10^{-6}$
Apparent density, g/cm^3	2.2	-
Relative density, %	97	-
Thermal conduction, cal/cm·s·deg	0.496	0.0019
Elastic modulus, kg/cm^3	$31 \cdot 10^4$	-
Flexural strength, kg/mm^2	19.25	-
Tensile strength, kg/mm^2:		
25°C	4.12	-
1650°C	5.60	
2000°C	7.63	-
2200°C	8.22	-

In comparison with properties of the usual hexagonal boron nitride (see Table 92), pyrolytic nitride possesses very high thermal conduction in the "c"-direction, considerably higher strength properties and a negative coefficient of thermal expansion at temperatures of 25-700°C (in the "a"-direction).

With respect to the rate of oxidation pyrolytic boron nitride is more stable as compared to pyrographite and also to pyrolytic boron carbide (Fig. 111) [714].

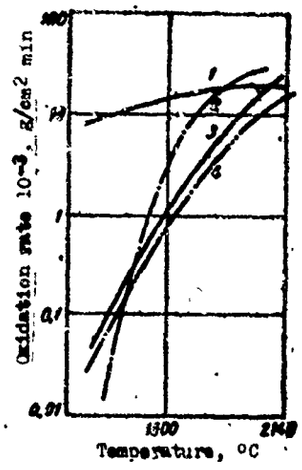

Fig. 111. Rate of oxidation of different pyrolytic materials 1 – pyrographite; 2 – pyrolytic B_4C; 3 – pyrolytic BN; 4 – pyrolytic alloy BN-C.

2. Aluminum Nitrides

The first published work on compounds of aluminum with nitrogen was in 1862 [571]. Further investigations of conditions of producing properties of these compounds are described by Mellor [572].

Essentially in all these works only one compound was revealed – AlN, which is sometimes ascribed to the formula Al_2N_2.

Aluminum nitride AlN is crystallized in a hexagonal lattice of wurtzite type. According to different data values of lattice constants vary within limits of a = 3.10-3.13 and c = 4.93-4.98 Å depending upon the degree of cleanness of the specimens [573].

Practice nitrogen is not dissolved in aluminum [602, 603, 604].

Physical properties. Powdery aluminum nitride is usually a white color, single crystals are watery white (transparent), and with contamination by impurities of aluminum hydroxycarbide Al_2OC the nitride obtains a blue or bluish color (in this case the content of the hydroxycarbide reaches 4-7%).

Data on the melting point of AlN are very contradictory (from 2000 to 2500°C), which is understandable since aluminum nitride is decomposed up to the achievement of the melting point on components, and temperature of the beginning of the decomposition is determined by peculiarities of conditions of the carrying out of the determination of the "melting point" [573, 574]. Hardness on Mohs mineralogic scale is determined also in a wide interval from 5 to 9-10 units), and the Knoop hardness (microhardness according to a load of 100 g) on the average consists about 1200 kg/mm^2. The impurity of hydroxycarbide does not change this mean value [573]. Physical properties of the aluminum nitride are most fully investigated in [575, 1100]; the samples contained up to 4% C, apparently, in form of hydroxycarbide. The temperature dependence of the electrical resistance is typical for semiconductors and dielectrics (Fig. 112), and the calculated width of the forbidden band of AlN is equal to $\Delta E = 4.26$ eV. Figure 113 shows the temperature dependence of the coefficient of thermal conduction. According to the magnitude of electrical resistance and theoretical value of the Lorenz number for semiconductors, the electron component of thermal conduction is calculated, which proved to be equal for 673°K to $4.6 \cdot 10^{-15}$ and at 1473°K – $2.5 \cdot 10^{-7}$ W/m·deg. Figure 114 shows the frequency dependences of the dielectric constant and dielectric-loss angles.

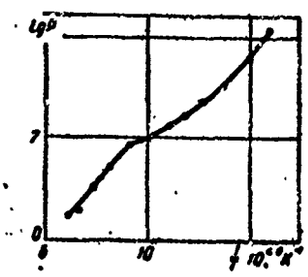

Fig. 112. Temperature dependence of the electrical resistance of AlN.

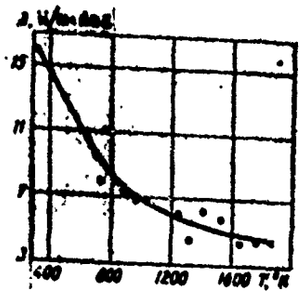

Fig. 113. Temperature dependence of the coefficient of thermal conduction of AlN.

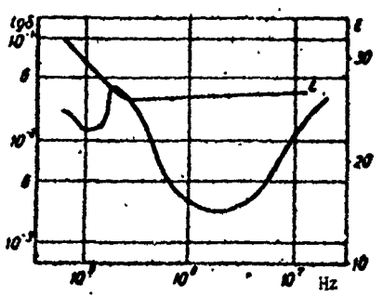

Fig. 114. Frequence dependence of the dielectric constant and dielectric-loss angle of AlN.

The analogy of electrical properties of AlN and Al_2O_3 is noted [573]. The dielectric constant at room temperature is 8.5, which is close to the value of the dielectric constant of Al_2O_3, for which its value is between 9 and 10. The dielectric constant of AlN rapidly increases with temperature at low frequencies and more slowly at high frequencies, so that at a frequency of $8.5 \cdot 10^9$ s^{-1} the change in the dielectric constant with temperature is very insignificant. Figures 115 and 116 shows the change in the dielectric constant and factor of dielectric losses with frequency and temperature. The distinction in these values from values of the dielectric constant shown in Fig. 114, according to data of [575], is connected with the contamination in the latter case of aluminum nitride by carbonitride. At low frequencies dielectric losses rapidly increase with temperature; however, a frequency of $8.5 \cdot 10^9$ s^{-1} the change with a temperature up to 500°C occurs slowly. At room temperature the loss factor is within 0.01-0.001, whereas for Al_2O_3 it is within 0.001 to 0.0001. At high temperatures and low frequencies, loss factors of AlN and Al_2O_3 are comparable, whereas at high temperatures and frequencies the scattering for Al_2O_3 is much lower.

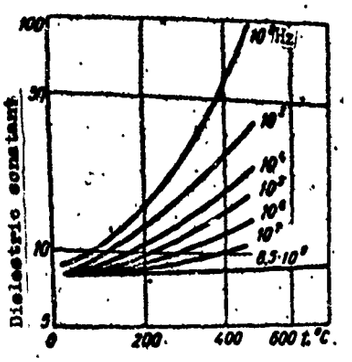

Fig. 115. Temperature dependence of the dielectric constant of AlN.

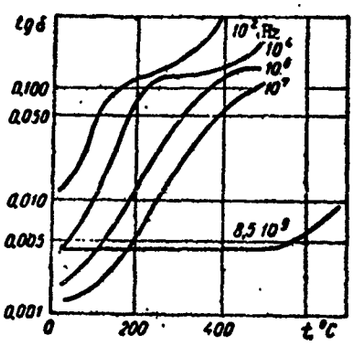

Fig. 116. Temperature dependence of the dielectric-loss angle of AlN.

Physical properties of aluminum nitride show that AlN is a typical dielectric with large width of the forbidden band and high electrical resistance, reaching, according to [574], up to 10^{20} Ω·cm. Calculation of the electron component of thermal conduction shows that thermal conduction is carried out only by lattice vibrations. Since for nonpolar solid dielectrics the relation $\varepsilon = n^2$, where ε – dielectric constant, n – refractive index (for AlN: $\varepsilon = 8.5$, $n = 2.13$, i.e., this relation is not fulfilled), then polarization of the nitride cannot be explained by only one electron component, and it, apparently, bears an ionic nature. Work [575] gives the following concepts about the mechanism of the formation of the bond in aluminum nitride. One of the electrons of nitrogen passes to an aluminum atom with the formation of such electron configurations: Al^- $2s^2 3s^2$; N^+ $2s^2 2p^2$. In compounds with a structure of the wurtzite type, every metal atom is surrounded by four nonmetal atoms located at

equal distances from it on vertexes of a regular tetrahedron (in AlN this is somewhat distorted). Thus, for every atom there must be four equivalent bonds, each of which is carried out by s-p-electrons proceeding one at a time from each atom. Such bonds of the covalent type, strengthened by ionic bonds superimposed on them, lead to the high rigidity of the lattice, which determines the small value of the coefficient of thermal expansion and high values of the modulus of normal elasticity, characteristic temperature and phonon component of thermal conduction.

Such a diagram is in general, correct; however, taking into account s → p-transitions it is necessary to consider that the configuration of part of atoms of aluminum and nitrogen has the form sp^3. Furthermore, together with the transition of an electron from an atom of nitrogen to an atom of aluminum there occurs the transition of valence electrons from part of aluminum atoms to nitrogen atoms with the formation here of configurations Al $2s^2 2p^6$ and N $2s^2 2p^6$, which conditions the presence of a fraction of the ionic bond in aluminum nitride.

In work [576] for aluminum nitride in the absence in the spectral region 2.5-5 eV of the absorption edge, a larger value of the width of the forbidden band ($\Delta E > 5$ eV), and on the other hand, in [577], where optical and electrical properties of AlN are investigated, it is shown that $\Delta E \approx 3.8$ eV. In this work it is established that the main absorption band lies in the ultraviolet region with the border at 3200 Å. In the same region weak photo-conductivity and the formation of photo-emf are observed.

The width of the forbidden band of AlN is close to bands of SiC and ZnO, which have a similar structure and close values of indices of refraction (atoms of Si can replace Al atoms, and atoms of C or O – atoms of nitrogen).

Two absorption bands are revealed in the region 0.60-0.65 μm and near the ultraviolet part of the spectrum, which explains the color of the crystals and indices the existence of two groups of impurity levels with average activation energies ∿2 and ∿3.2 eV. The third band is revealed in the ultraviolet region, which corresponds to the third group of levels with an activation energy of ∿0.6 eV. During the action of ultraviolet rays of aluminum nitride gives short-term liminescence (yellow or yellow-green) in the interval λ = 0.45-0.65 μm. A photoelectrical effect is observed only wit' very intense irradiation by light of an electrical arc.

In work [1016] the photoconductivity is single crystals of AlN induced by the laser is investigated.

A thorough investigation of the AlN structure is carried out in [578]. It is shown that the AlN structure differs from the ideal wurtzite structure, since the ratio c/a is equal to 1.600 instead of 1.633 , and parameter U, which determines the distance Al-N along the trigonal axis, is equal to 0.385 instead of 0.375. Compression of the tetrahedron along the C axis in the structure of AlN leads to a certain distortion of the correct tetrahedral location of bonds Al-N. An increase in the value of parameter U indicates the fact that the center of electron density in every atom does not coincide with the center of the tetrahedron formed by its nearest neighbors, and that the atom is displaced along the C axis to the base of the tetrahedron by 0.05 Å. Consequently, angles between bonds Al-N vary from 107.7 to 110.5°, and distances of Al-N vary from 1.885 to 1.917 Å.

In the investigation of growth spirals and polytypes of AlN crystals obtained from a gas phase [579], the presence of spirals known for SiC is shown (Fig. 117), and they vary from polygonal to almost round, and the height of steps of layers of the growth consists several hundreds of Å. In contrast to the isostructural of SiC and ZnS for aluminum nitride, polytypic structures were not determined roentgenographically, and therefore growth spirals cannot be explained on the basis of a polytype, as is done, for example in the case of silicon carbide.

Fig. 117. Growth spiral on plane (0001) AlN × 160.

Thermodynamic properties of aluminum nitride are studied in most detail in [580], and results of the investigation are given in Table 97. The change in heat content in the region 298-1800°K $H_T - H_{298} = 10.98T + 0.4 \cdot 10^{-3}T^2 + 3.58 \cdot 10^5 T^{-1} - 4.51$, and the temperature dependence of the heat capacity $c_p = 10.98 + 0.80 \cdot 10^{-3}T - 3.58 \cdot 10^5 T^{-2}$. The change in the isobaric potential of reaction Al + 1/2 N_2 = AlN with temperature is the following:

T, °K	298	1000	1100	1400	1500	1700	1900	2000
$-\Delta F^\circ$, kcal	68.15	50.20	47.40	39.00	35.25	30.70	25.20	22.44

Table 97. Properties of aluminum nitride.

Characteristic	AlN
Content, wt. %	34.9
Crystal structure	Hexagonal of wurtzite type
Lattice constants, Å:	
a	3.104 [581]
c	4.965
c/a	1.600
Density, g/cm³:	
X-ray	3.27 [583]
pycnometric	3.12
Melting point, °C	2400 [578] is decomposed

Table 97 Cont'd.

Characteristic	AlN
Heat of formation, kcal/mole	76.47 ± 0.20 [582]. see also [580]
Entropy, cal/deg·mole	4.8 ± 0.20 [580]
Thermal conduction, cal/cm·s·deg:	
200°C	0.072 [578]. see also [575]
400°C	0.060
600°C	0.053
800°C	0.048
Coefficient of thermal expansion	
$10^6 \cdot deg^{-1}$:	
25-200°C	4.03 [578]. see also [585]
25-600°C	4.84
25-1000°C	5.64
25-1350°C	6.09
Specific electrical resistance, Ω·cm	
293°K	$>10^{13}$ [575]
673°K	$2.25 \cdot 10^{11}$
773°K	10^9
873°K	$8 \cdot 10^7$
1073°K	$4 \cdot 10^6$
1173°K	$7 \cdot 10^5$
1273°K	10^5
1373°K	$4 \cdot 10^4$
1473°K	$9 \cdot 10^3$
Width of forbidden band, eV	3.8 [577] to >5 [576]
Dielectric constant	8.5 [573]
Refractive index	2.13 [583]—2.20 [1003]
Radiation factor (λ = 655 μm):	
800-2000°C (in a medium of argon)	0.80 [340]
800-1400°C (in a vacuum)	0.85 [340]
Mohs hardness	~9 [573]
Knoop hardness kg/mm²	1230 [573]
Elastic modulus, kg/mm²	
20°C	35050 [573]
1000°C	32300
1400°C	28100

Table 97 Cont'd.

Characteristic	AlN
Tensile strength with rupture, kg/mm^2:	
25°C	27 [573]
1000°C	~19
1400°C	12.7
Vapor pressure, mm Hg:	
1000°K	$5 \cdot 10^{-11}$ [610]
1200°K	$2 \cdot 10^{-8}$ [610]
1400°K	$1 \cdot 10^{-5}$ [610]
1600°K	$0{,}9 \cdot 10^{-4}$ [610]
1760°K	1 [150, 1101]
2173°K	14 [45]
Energy of dissociation, kcal/mole	82–187 [611]

In work [584] mass spectrometric investigations of AlN evaporation is conducted, is determined and the approximate heat content $\Delta H_{298} \approx -63$ kcal/mole, which is considerably below that calorimetrically defined.

The strength of aluminum nitride at high temperatures (of the order of 1400°C) can be compared with the strength of oxide ceramics, and at the usual temperature it somewhat yields to the oxides. The thermal conduction of technical AlN is one order less than thermal conduction of dense carborundum and 2-3 times higher than thermal conduction of ceramics of Al_2O_3 [573]. Thermal expansion at average temperatures somewhat exceeds the thermal expansion of carborundum. The resistance to thermal shock is high, so with thermal cycling 2200-20°C articles of BN are not destroyed for several cycles. After 30 cycles of heating for 2.5 min up to 1400°C and rapid cooling to room temperature in air the loss of strength is 12% [565].

Chemical properties. Articles from aluminum nitride are slowly dissolved in hot mineral acids (Table 98, [578]).

Table 98. Corrosion of hot-pressed aluminum nitride in water and mineral acids (time of the test — 72 h).

Medium	t, °C	Corrosion rate, mm/year
H_2O	100	14
HCl (concen.)	72	320
HCl (1:1)	100	570
H_2SO_4 (concen.)	305	180
H_2SO_4 (1:1)	145	550
HNO_3 (concen.)	120	150
HNO_3 (1:1)	111	200
HF (concen.) + HNO_3 (concen.)	57	160
HP (1:1)	57	215
HF (1:1)	57	170 (single AlN crystals)

Hydrochloric, nitric, and sulfuric acids, and aqua regia in the cold act very weakly on powdery aluminum nitride [610]. With heating in H_2SO (1:1) aluminum nitride is decomposed completely in four days ($2AlN + H_2SO + 6H_2O = 2Al(OH)_3 + (NH_4)_2SO_4$). Cold hydrofluoric acid also does not act on AlN. Concentrated hot solutions of alkalis decompose the aluminum nitride with the separation of ammonia:

$$AlN + 3H_2O + OH^- \rightarrow Al(OH)_4^- + NH_3.$$

Compact aluminum nitride is considerably more resistant to the action of acids and alkalis than that of the powdery. Thus, compact AlN samples are absolutely stable with boiling in concentrated sulfuric acid, and with difficulty they yield to the effect of boiling nitric and hydrochloric acids. The stability increases in diluted acids and solutions of alkalis [612].

Dry halogens slowly act on the nitride, and chlorine starts to decompose at a temperature of 760°C with the formation of $AlCl_3$ [610], and dry hydrogen chloride practically does not act. Upon heating with sulfur and vaporous carbon bisulfide the aluminum nitride is decomposed partially, by vapors of sulfur chloride AlN is decomposed rapidly, the phosphorus partially it decomposes, and the

PCl_3 does not act. The reaction with carbon starts at a temperature of 1200°C. Sodium peroxide decomposes aluminum nitride with the formation nitrates, and completely and rapidly AlN is decomposed by lead bichromate [572].[2]

The oxidation of powder in air is started at a temperature of 1200°C [574], and according to data of [612] – at 900°C. The heat of the reaction of the oxidation $AlN_{TB} + 3/4\ O_2 = 1/2\ Al_2O_3 + 1/2\ N_2$ consists $-\Delta H^\circ_{298} = 124.6 \pm 0.0370$ kcal [580].

The corrosion rate during the action of hot gases depends on the density of articles from nitride. It is shown [578, 585] that with oxidation of the sintered nitride at 1200°C for 1 hour 11% of the nitride is turned into aluminum oxide, and with oxidation of the hot-pressed sample at 1400°C for 30 hours only 1% of the nitride is transformed into the oxide. Table 99 gives data on the corrosion of hot-pressed, dense aluminum nitride in different gaseous environments.

Table 99. Corrosion of hot-pressed aluminum nitride in gaseous media.

Medium	t, °C	Time, h	Transition of nitride into an oxide or other compound, %
Air	1000	30	0,3
Air	1400	30	1,3
Air	1700	4	10,6
Oxygen	1400	30	0,9
Dry vapor	1000	30	0,3
Chlorine	500	30	0,1
Chlorine	700	30	19,2
Hydrogen	1700	4	Does not react

Melted aluminum (up to 2000°C) gallium (up to 1300°C), boric anhydride (up to 1400°C) does not act on aluminum nitride [585]. AlN is stable in a mixture of molten cryolite and aluminum for 66 h at 1200°C [578], and melted boric anhydride at a temperature of 1000°C causes after 4 h a loss in weight of only 0.02%.

Aluminum nitride reacts with basalt (1400°C; 0.5 h), with copper matte (1300°C; 5 h), slower – with nickel matte (1250°C; 5 h), weakly – with copper slag (1300°C; 5 h), and it does not react with the melt of NaCl + $BaCl_2$ [541].

The high stability is revealed of aluminum nitride in relation to the many semiconductor compounds, in particular, to semiconductors of the type $A^{III}B^{V}$. In work [610] it is shown that it is especially stable with respect to the molten GaAs, which permits using containers of aluminum nitride for the purification and production of single crystals from this semiconductor.

It is also stable in contact with graphite up to high temperatures, and with tungsten and molybdenum – up to 1800°C [610].

Methods of production. Numerous methods of production of aluminum nitride used both in the laboratory and in industrial scales have been developed.

1. Direct nitration of aluminum. Aluminum nitride was obtained for the first time in 1862 by the action of nitrogen on aluminum at a temperature of 700°C [571].

The kinetics of the nitration of aluminum was investigated in the range of temperatures of 530-625°C [75]. At low temperatures down to 580°C the nitration obeys the linear law, and at higher temperatures – the parabolic law.

In the linear region of temperatures the constant of the rate of nitration is expressed by $K = 58 \exp(-17{,}900/RT)$ mg/cm^2·h, and in the parabolic region – $K = 4.2 \cdot 10^{10} \exp(-23{,}700/RT)$ mg/cm^2·h.

The constant of aluminum oxidation in the linear region of temperatures $K = 2.34 \cdot 10^{11} \exp(-47{,}700/RT)$, and in the parabolic – $K = 1.35 \cdot 10^{3} \exp(-22{,}800/RT)$, i.e., in both cases the rate of oxidation is considerably higher than the rate of nitration.

A peculiarity of the nitration of aluminum powder is the formation on the surface of particles of oxide films (γ-Al_2O_3), which depart, apparently, as a result of the formation of lowest volatile aluminum oxides: $Al_2O_3 + 4Al = 3Al_2O$. Disturbance of the film with reconstruction of Al_2O_3 into Al_2O permits the nitrogen to penetrate to the juvenile surface of aluminum and to conduct nitration.

In this case a thin AlN film, poorly permeable for nitrogen will be formed, which causes the transition from the linear law of nitration to the parabolic at high temperatures, and sometimes the film already starts to be formed.

Thus, to accelerate the reaction of the formation of aluminum nitride, it is necessary to use the finest aluminum powders, which, although they are more oxidized they, nonetheless, permit more completely conducting the reaction of nitration with the formation of nitride. With nitration the sintering of the aluminum powder, which reduces the reaction surface simultaneously occurs. To prevent sintering, step conditions of nitration are used, and these are calculated on the fact that already at low temperatures there is observed coating of the particles by nitride films, which will delay sintering of the powder.

The aluminum nitride can be produced by the nitration of aluminum powder (PAK-4) [586]. For the production of aluminum nitride of stoichiometrical composition the aluminum powder is treated by nitrogen at 800°C for 1 hour (rate of rise of temperature up to 800°C is 10 deg/min) with mixing of the formed product and repeated nitration at 1200°C for 0.5-1 hour (with the rate of rise of temperature up to 1200°C is 40 deg/min). Technical aluminum nitride (with a content of 33% N) is produced by means of single nitration at 1200°C with the rate of rise of temperature of 10 deg/min.

The slow rise in temperature and also step conditions of the nitration with intermediate grindings permits avoiding the sintering of the aluminum powder prior to nitration.

Conducted in work [587] is the nitration of aluminum powder (brand PO-1) and aluminum powder with a "lining" from aluminum nitride, which has due to the fineness of particles a greatly developed surface and prevents sintering of aluminum particles with each other. It was found that an introduction of 30% AlN into the charge with the aluminum powder is sufficient for the production with monophase nitration of qualitative aluminum nitride (at 1200°C lasting 1 h). However, here friable, easily pulverized sinters are formed; the productivity of production nitride decreases due to the cycle of 30% nitride of aluminum introduced into the fresh charges.

The authors [558] investigated more specifically the nitration of powder and aluminum powder. It is shown that the formation of aluminum nitride with the nitration of powder PAK-4 starts already at a temperature of 400°C; at 500°C up to 15% the powder becomes a nitride, and at 600°C – up to 20% (with a four-hour holding time). An especially intense formation of nitride occurs at 720-730°C, which requires the supply of additional quantities of nitrogen. The temperature in the reactor after 1-1.5 min increases up to 1400-1500°C, and in 15-20 min the reaction is practically finished.

The formation of aluminum nitride with the nitration of aluminum powder PA-4 starts at 600°C, but the quantity of the produced nitride here is very insignificant and up to 800°C comprises not more than 1%. With an increase in temperature above 800°C frequently sintering of the powder is observed, and maximum yield of the nitride can be produced equal to only 50-60%. Further nitration is prevented by fusion of the aluminum and sharp reduction in the reaction surface.

With a decrease in coarseness of particles of the aluminum powder from 160-250 to 70-100 μm, the quantity of the nitride produced is increased rather sharply.

Since with an increase in temperature the decrease in free energy of the reaction of the formation of nitride decreases, then one should have expected a more complete passage of the reaction with a lowering of the temperature. Results of the investigations show that, conversely with a temperature rise the reaction is more complete.

Such noncorrespondence is explained by the fact that the rate of reaction of the formation of AlN essentially depends on the diffusion rate of nitrogen to aluminum. The dense film of aluminum oxide on powder particles is a substantial obstacle of the diffusion of nitrogen. This is confirmed by experiments of Smittels and Ransley [589], who showed that with the removal of the oxide film from the aluminum surface the diffusion rate of hydrogen is increased by ten times. The diffusion rate of nitrogen both through the oxide film and through the nitride film sharply increases with temperature, and this leads to a greater rate of nitration, covering the deceleration of the reaction of aluminum with nitrogen, resulting from purely thermodynamic considerations. Since the reaction of the formation of aluminum nitride is accompanied by a high thermal effect, then the first portions of nitrogen penetrating through the film to the aluminum cause a great increase in temperature, which in turn causes an increase in the diffusion rate of nitrogen, i.e, reaction has a unique "chain" character. If at the beginning of this process external heating is ceased, then the reaction continues in the cold," passing with sufficient delivery of nitrogen up to the end. The reaction of the formation of nitride from the powder PAK-4 obtains a "chain" character at a temperature of 720-730°C, and from aluminum powder – at a temperature of above 800°C.

Therefore, in [588] in production of aluminum nitride in a current of nitrogen from powder PAK-4 it is recommended to raise the temperature before the beginning of the spontaneous reaction, which passes up to the end for 30-40 minutes. With nitration of the aluminum powder the spontaneous reaction cannot be finished and is stopped with the formation of 50-70% nitride.

In work [590] the effect of the pressure of nitrogen on the process of nitration of aluminum powder PA-4 and aluminum powder PAK-4 was studied. With nitration of the powder an increase in pressure of the nitrogen promotes the formation of nitride (Fig. 118). With a temperature rise the positive effect of an increase in pressure on the formation rate of nitride decreases and at 665°C for the time of the holding of 120 min, and at 690°C for the holding time of 60 min it becomes negative. Other things being equal the reaction of the formation of aluminum nitride is accelerated with the lowering of pressure.

With nitration of powder PA-4 the increase in pressure of the nitrogen accelerates the reaction of AlN formation (Fig. 119); see also [1102].

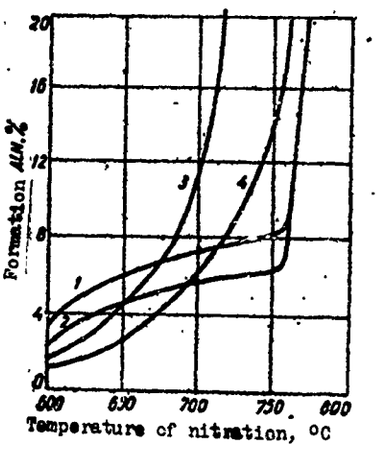

Fig. 118. Temperature dependence of the yield of aluminum nitride with nitration of the powder PAK-4: 1 – pressure of nitrogen, 3 at., holding time, 120 min; 2 – pressure of nitrogen, 3 at, holding time, 60 min; 3 – pressure of nitrogen, 2 at., holding time, 120 min; 4 – pressure of nitrogen, 2 at, holding time, 60 min.

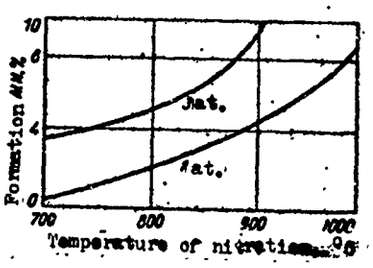

Fig. 119. Dependence of the yield of aluminum with the nitration of powder PA-4 on the temperature and pressure of the nitrogen.

Such an unexpected effect of pressure on the process of nitration of aluminum powder can be preliminarily explained in the following way. Before entering in the reaction with aluminum, the nitrogen should diffuse through the oxide film γ-Al_2O_3, available for each particle of aluminum, and also through the film of the formed aluminum nitride. The quantity of gas diffusing through a unit of area per unit length per unit time through a substance is determined by the formula of Smithells [591]:

$$D = \frac{n}{d}\sqrt{p}\cdot e^{-\frac{E_D}{2RT}},$$

where n – constant, d – thickness of the layer of the substance, p – pressure of the gas, E_D – activation energy (heat of diffusion). From the given expression it is clear that the diffusion rate is proportional to $\sqrt{p}$ and with an increase in temperature should increase sharply. As has already been shown the rate of reaction of the AlN formation is limited by the diffusion rate of nitrogen through the oxide-nitride film to aluminum. Up to the melting point of aluminum the law $\sqrt{p}$ is observed. With melting of surface the aluminum tries to be reduced due to forces of surface tension, and of aluminum particles, having the same form of leaves (PAK-4), drops, dendrites, press cakes (PA-4), try to assume a spherical form, and this process is prevented by an oxide-nitride film. With a temperature rise the strength of the film decreases, and at a definite temperature the surface tension starts to prevail over the strength of the film, the latter breaks, and the melted aluminum pours out from the particles. At the time of the yield of the drop of aluminum from the oxide-nitride shell, there occurs almost an instantaneous nitration of the aluminum, since the magnitude of these drops in the case of the thin powder PAK-4 is very small.

The thinner the film, the smaller the forces necessary for its destruction, and, consequently, the lower temperatures of the process. Inasmuch as prior to the melting of aluminum an increase in pressure

of the nitrogen promotes the formation of aluminum nitride, then during the process of nitration at these temperatures a thicker and more durable film will be formed. For the destruction of such a film higher temperatures are required, and at these temperatures the strength of the film becomes less than that of forces of the surface tension of the drop of aluminum.

With nitration of the powder PA-4 the mechanism of the process of nitration in general remains the same as that with nitration of the powder PAK-4, but drops of aluminum, produced after destruction of the film, here are considerably larger. Therefore, the drops succeed in being nitrated only partially from the surface and have a tendency toward fusion (experimentally large particles with a dimension of up to 2-3 mm are observed). Due to the fusion of the drops the surface is sharply reduced and to much smaller as compared to that of the powder PAK-4, and, accordingly, the rate of nitration decreases. Further nitration occurs as a result of the diffusion of nitrogen through the film and obeys to the law $y\sqrt{p}$ (Fig. 119).

To accelerate the process of production of aluminum nitride by direct nitration of metal, in a patent [592] it is proposed to introduce into the aluminum powder 5% KF as a catalyst. The mixture of pure powdery aluminum (110-220 meshes) and the catalyst KF is heated in a medium of nitrogen at a temperature of below the melting point of aluminum before the beginning of the reaction of nitration, and then the temperature is increased up to the melting point of aluminum prior to the termination of the formation of AlN. In the product obtained 90-95% AlN is contained and the yield consists 95-100%. The process of nitration is considerably accelerated by the addition to aluminum of 5% KHF_2 [246] or 1% NaF [619].

In work [585] method of producing aluminum nitride is proposed by the burning of aluminum in oxygen with subsequent substitution of oxygen with nitrogen at high temperatures. A nitride of high

purity is produced by the atomization of the aluminum by an electrical arc in a medium of nitrogen [585]. The original method of producing aluminum nitride by fusible aluminum in a suspension (in a high-frequency field) in nitrogen is described in [1103]. Crystals of aluminum nitride of up to 30 mm long and 0.5 mm in diameter will be formed with the evaporation of aluminum in nitrogen at a temperature of 1800-2000°C [573].

For the production of single nitride crystals, there is also used the method of sublimation from a gas phase at 1900°C [593-595], which is similar to the method of producing single crystals of silicon carbide. Crystals of a greenish-blue color with dimensions of up to 2 mm will be formed.

Single crystals of aluminum nitride are produced by the transfer during 24 hours of the mixture of nitrogen and argon over aluminum melted at 1500°C placed in a corundum boat located in a corundum pipe [601, 614]. On walls of the latter, having a temperature of about 1450°C, single AlN crystals grow in the form of plates and needles (dimensions, accordingly, are 1 × 1 and 4 × 0.1 × 0.1 mm). It is indicated that the production of larger single AlN crystals is possible with the help of gas transport reactions [614].

Very pure (up to 99.999%) AlN powder will be formed [619] with the heating of the aluminum powder (99.999%) in crucibles of AlN in a medium of thoroughly purified nitrogen. The reaction passes at a temperature of 1600°C and pressure of 100 at.

Sometimes for the removal of impurities an additional treatment of the produced aluminum nitride by chlorine at 600°C.

In the action of ammonia on aluminum nitride will also be formed: $2Al + 2NH_3 \rightarrow 2AlN + 3H_2 + 2.57$ kcal [6].

2. Reduction-nitration of aluminum oxide. In work [596] the possibility of producing aluminum nitride is indicated by the action of ammonia at a temperature of 1000°C on finely pulverized aluminum oxide, formed with decomposition at 650°C of aluminum acetate. A somewhat more detailed investigation of this process is carried out in [597], where it is shown that ammonia reacts very slowly with aluminum oxide at 1000°C with the formation of aluminum nitride. At higher temperatures (about 2000°C) with smelting the appearance of two phases is revealed: γ-phase and δ-phase. The region of homogeneity of the γ-phase at a temperature of 1700°C extends from 68 to 84% Al_2O_3 (32 or 16% AlN), has the structure of spinel close to the structure of Al_2O_3. The δ-phase is less rich in nitrogen (approximate composition 93% Al_2O_3, 7% AlN), and the structure is close to the structure of aluminum oxide. The γ- and δ-phase represent aluminum hydroxynitrides (in the diagram of the system Al_2O_3-AlN) and are produced with the reaction of aluminum oxide and aluminum nitride in a solid state.

3. Production of aluminum nitride from a gas phase (methods of thermal decomposition). For the first time in 1938 in [598] it is mentioned that it is possible to obtain aluminum nitride by the decomposition of $AlCl_3 \cdot 6NH_3$ through the stage of formation of the intermediate product $AlCl_3 \cdot NH_3$. Renner [574] also produced aluminum nitride by thermal decomposition $AlCl_3 \cdot NH_3 \rightarrow AlN + 3HCl$ in the apparatus shown on Fig. 120. In a long quartz tube on a thin quartz tube there is suspended a graphite washer, which is heated by a current of high frequency with the help of a water-cooled copper spiral. The basic quartz tube is filled in the lower part by a definite quantity of $AlCl_3 \cdot NH_3$, which is heated by a furnace moving in the tube to a definite pressure of $AlCl_3 \cdot NH_3$ vapors. At sufficiently high temperatures with decomposition, crystals possessing clearly expressed edges will be formed (Fig. 121). This method was investigated again in works [1102, 1104, 1105].

Fig. 120. Apparatus for the production of aluminum nitride from a gas phase: 1 – quartz tube; 2 – graphite disk; 3 – copper inductor; 4 – furnace.

Fig. 121. AlN crystals produced from a gas phase.

Researchers [596] carried out such a method of producing AlN by the deposition of aluminum nitride on a tungsten thread by the decomposition of mixtures of vaporous $AlCl_3$ with argon and ammonia. At temperatures of 800-1100°C the residue of nitride represents a solid layer of little thickness durably united with the thread. At a temperature of the thread above 1200°C the deposit obtained is friable, nonuniformly covers the thread and is weakly connected with it, and its structure is typically dendritic.

It is possible to produce aluminum nitride by the thermal decomposition of $Al(CH_3)\cdot NH_3$ at 200-300°C [599]. The nitride produced is very unstable, is easily hydrolyzed on humid air with the separation of ammonia, and full hydrolysis is completed in 48 hours [596].

With thermal decomposition of $(NH_4)_3AlF_6$ in a current of ammonia at a temperature of 500-C, pure aluminum nitride is formed [274]. The color and chemical behavior of it greatly depend on the temperature of the preparation (at 500-600°C the color of AlN changes from brown to olive-green, at 700-800°C – black-green with a violet gloss). Aluminum nitride produced by such method is less active in a chemical relation than AlN, formed by the nitration of aluminum.

4. Reduction of aluminum oxide with simultaneous nitration. For the industrial production of technical aluminum nitride, the so-called Serpek method [6, 110, 600, 596] was used, which was found on the reaction

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO.$$

The reaction is endothermic, it occurs with the absorption of a great quantity of heat, and the temperature the reduction-nitration is of the order of 1600-1800°C. In the presence of iron, which acts as a catalyst, the temperature of the process drops to 1400°C. In industry this method (intended for the subsequent decomposition

of aluminum nitride by steam with the formation of aluminum hydroxide or soda with the formation of sodium aluminate) is carried out in revolving furnaces 60 m long and 3-4 m in diameter.

5. Other methods of producing aluminum nitride.

Aluminum nitride is obtained by the heating of thin powder of aluminum phosphide in a slow current of dry ammonia for 1-2 hours at a temperature of 1000-1100°C [599]

$$AlP + NH_3 \rightarrow AlN + 1/4P_4 + 3/2H_2.$$

Here an amorphous AlN powder will be formed, and only after multihour heat treatment at 1100°C are lines characteristic for the hexagonal aluminum nitride roentgenographically revealed.

Production articles from aluminum nitride. Articles from aluminum nitride are produced by different methods: 1) by sintering of preliminarily pressed billets from powder of aluminum nitride; 2) by reaction sintering of billets from aluminum powder in nitrogen or ammonia; 3) by hot pressing of powder of aluminum nitride.

The first of these methods can be carried out according to the technology described in detail in [605]. Nitride powder in a mixture with aluminum powder or powder in a quantity of 10% are pressed with a plasticizer (5-6% addition of 5%-solution of synthetic rubber in gasoline), the billet is dried and baked according to defined conditions with the final temperature of sintering of 1900°C in a medium of nitrogen. With sintering the aluminum powder passes into a nitride [609], articles will be formed from aluminum nitride with a porosity of 12-16% [586], and according to [609] – even a porosity of 2-6%. A similar method is described in a patent [606] where the powder of aluminum nitride is mixed with a small quantity of aluminum and a binder, which can be cerezine, ozocerite or polyglycol, and also with a plasticizer – trichlorethylene; it is pressed and baked in a medium of nitrogen at a temperature of above 1400°C. It is

possible to produce an article from AlN by the preliminary activation of the pressings by heating at a temperature of 450°C in an oxidizing medium with subsequent sintering in a nitrogen-containing medium at ~1400°C. Based on the same principle of sintering mixtures of powders of nitride and aluminum are recommendations of patents [607, 608].

Billets from aluminum nitride can be prepared by slip casting [585]. Since the aluminum nitride hydrophobic, then as a suspending medium dioxan can be used.

Good results are given by hydrostatic pressing of powder of aluminum nitride with subsequent sintering in a medium of argon at 1950-2050°C [585].

The second fundamental method of producing articles from aluminum nitride is reaction sintering of billets from aluminum powder in a medium of nitrogen. This method, founded on the nitration of billets from aluminum powder, pressed under a pressure of 8 t/cm^2, does not permit production of an aritcle with a density above 50-60% of the theoretical [234].

Hot pressing is carried out under a pressure of 300 kg/cm^2 at temperatures of the order of 2000-2100°C with production of articles having practically zero porosity [605] or of the order of 1.5% [609].

3. Gallium Nitrides

In the gallium-nitrogen system one compound is revealed – gallium nitride GaN. Its structure was first investigated in work [613], where it is shown that GaN possesses a hexagonal structure of the wurtzite type.

Physical properties. Gallium nitride belongs to semiconductor compounds of the type $A^{III}B^{V}$, and it differs from other compounds

of gallium of such type (phosphide, arsenide, antimonide, stibnide, bismutide) by the higher melting points and sublimation and also by resistance to oxidation and action of chemical reagents. The width of the forbidden band of gallium nitride according to various measurements consists 3.25-3.6 eV [614], which corresponds to the high electrical resistance of nitride, which, according to Renner [574], consists 10-100 Ω·cm and according to data of [33], obtained on a purer preparation, – $4.0 \cdot 10^{8}$ Ω·cm.

The melting point of GaN is ∿1500°C [574], and the vapor pressure at a temperature of 1130°C reaches $4 \cdot 10^{-11}$ at. [617], which is confirmed by measurements conducted in [574], where it was assumed that nitride sublimates mono- or polymolecularly, without dissociation. However, in [613] it is affirmed that gallium nitride is thermally unstable and dissociates starting from temperature below 600°C and at 1000°C dissociates completely to gallium and nitrogen. At the same time according to values of free energy and heat of formation [617], it is possible to calculate the equilibrium pressure of $GaN_{газ}$ vapor, which at 1500°C proves to be equal to $4 \cdot 10^{-5}$ mm Hg, which is considerably lower than the vapor pressure of gallium ($2 \cdot 10^{-1}$ mm Hg). From these data it follows that gallium nitride not only does not dissociate but vaporizes not in the form of diatomic molecules and forms complex polymers in the vapors. Therefore, authors [616] investigated the composition of vapor over gallium nitride by the mass spectrometric method. It is shown that gallium nitride vaporizes basically in the from of dimers and does not dissociate (dissociation in vapors is possible only with additional excitations, for example, with collisions of polymers with electrons).

Gallium nitride possesses luminescent properties, in particular, in the investigation of cathodoluminescence on GaN powders two maxima of intensity are revealed at 3200 and 5200 Å [615, 614].

Gallium nitride is a superconductor with the transition point to superconductivity of 5.85°K, i.e., is as yet a rather rare combination of a superconductor and semiconductor [618]. Information on physical properties of GaN are given in Table 100.

Table 10C. Properties of gallium nitride.

Characteristic	GaN
Nitrogen content, wt. %	16.72
Crystal structure	Hexagonal, wurtzite type
Lattice constants Å:	
a	3.180 [31]
c	5.166
c/a	1.625
Density, g/cm^3	6.1
Melting point, °C	~1500 [614] (is decomposed)
Heat of formation, kcal/mole	24.9 [112]
Energy of dissociation, kcal/mole	72-101 [611]
Specific electrical resistance, Ω·cm	$4.0 \cdot 10^8$ [33]
Width of forbidden zone, eV	3.25-3.60 [33, 614]
Temperature of transition to superconductivity, °K	5.85 [618]
Vapor pressure at 1100°C at,	$4 \cdot 10^{-11}$ [617]

Chemical properties. Gallium nitride is resistant to the action of different chemical reagents [612]. With boiling sulfuric and nitric acid do not act on powdery nitride, and at the same time with solutions of alkalis it is rapidly and completely decomposed but more slowly than AlN by alkalis [574].

In air it begins to be oxidized (in the form of powder) at a temperature of 800°C, and oxidation is completed at 1200°C with the formation of Ga_2O_3 [612]. Hydrogen does not act on GaN [614].

Methods of production. Gallium nitride is produced by the heating of metallic gallium in a current of ammonia at a temperature of 1200°C [613].

According to Hahn and Juze [31], and also Johnson and his colleagues [62], gallium nitride can be produced by double heating of metallic gallium in a corundum boat in the rapid current of

ammonia for 2 hours at 1100°C with the crushing of the intermediate product produced after the first nitration. It is possible to produce gallium nitride by the decomposition ammonium flurogallate $(NH_4)_3GaF_6$ in a current of ammonia at 900°C [102]. According to Renner [574] gallium nitride is produced by the decomposition of salt $GaCl_3 \cdot NH_3$ at 900-1000°C.

In work [599] gallium nitride was produced by heat treatment of fine powder GaP or GaAs in a current of dry ammonia. The transformation of GaP in GaN starts at a temperature of 900°C, and full transformation in nitride occurs with heating for 2 hours 1000-1100°C. The GaAs with ammonia starts to react at 700°C, and the quantitative transition of arsenide in gallium nitride is observed for 1-2 hours at 1000°C. Cooling of products of the reaction is produced in a medium of ammonia. With the use of phosphide gallium nitride of yellowish color is produced, and when using arsenide – a white color.

Numerous methods of producing gallium nitride are given in [619].

A detailed investigation of conditions of the formation of gallium nitride is carried out in [620]. The difficulty of nitration of gallium is the formation by fusible gallium (m.p. 29.7°C) of the surface of the melt, which causes sharp reduction in the reaction surface. Therefore, multiple nitration with the production of nitride of a stoichiometrical composition is necessary. The authors [620] used scarifiers, which, being decomposed during heating, separate the gases mixing the liquid gallium and facilitate the access to it of the nitrating agent. The most successful scarifier is carbonate ammonium, with the decomposition of which there is separated ammonia, which participates in the loosening and in the process of nitration, and also CO_2, which greatly lossens the melt. Results of the investigations are shown in Fig. 122. Such a method permits producing with the ratio $Ga:(NH_4)_2CO_3 = 1:1$, with the use of ammonia

as the nitrating agent at a temperature of 1050-1200°C and holding time of 0.5-2 hours, the gallium nitride of exact stoichiometrical composition, with an 85-95% yield of gallium in the product of nitration.

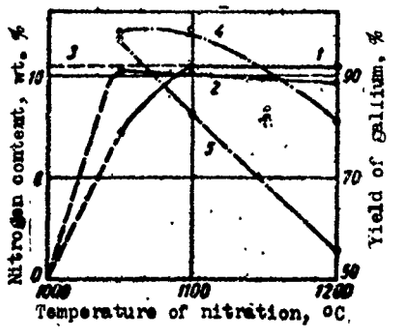

Fig. 122. Dependence of the content of nitrogen and yield of gallium in the product of nitration of metallic gallium in a mixture with ammonium carbonate on the temperature and time of nitration. Time of nitration: 1 — 1 h; 2 — 4 h; 3 — calculated content of nitrogen in GaN; yield of gallium into the product of nitration with nitration in the course of: 4 — 1 h, 5 — 4 h.

The method of obtaining of gallium nitride is developed by reduction of the gallium oxide by ammonia with simultaneous nitration [620]

$$Ga_2O_3 + 2NH_3 = 2GaN + 3H_2O.$$

With the use in this case of carbonate ammonium (1:1) as the scarifier nitride of calculated composition will be formed with prolonged holding at 1050°C with holding for 1-2 h at 1100-1200°C (Fig. 123). The GaN is also obtained by reduction of the gallium oxide by ammonia at 600-1100°C [615].

Both these methods are convenient for producing gallium nitride in large quantities.

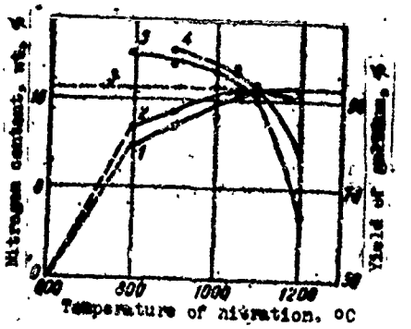

Fig. 123. Dependence of the content of nitrogen and yield of gallium in the product of nitration of gallium oxide in a mixture with ammonium carbonate on the temperature and time of nitration (designations are the same as those on Fig. 122).

Rabenau [619] indicates the possibility of production single-crystal GaN samples by means of sublimation of it at a temperature of 1000-1100°C. A more promising method is the growing of single GaN crystals from solutions, for example, nitride in gallium [614]. However, since the solubility is small (does not exceed 1-2%), the producing of more or less large single crystals by this method is improbable.

4. Indium Nitrides

Just as aluminum and gallium, indium forms one nitride — InN, which has the structure of wurtzite (a = 3.533; c = 5.693; c/a = = 1.611 [33]).

Physical properties. Indium nitride is a semiconductor, but properties of it in this respect have absolutely not been studied. In work [33] it is noted that InN has a metallic character with a resistance of the order of $4 \cdot 10^{-3}$ Ω·cm and temperature drag coefficient of $+0.00037\ deg^{-1}$. The authors [574] also indicate its good conductivity and resistance, which is considerably less than 1 Ω·cm. From these data it follows that InN is a semimetallic compound. Theoretical appraisals show the width of the forbidden band of indium nitride, if it is a semiconductor, should be of the order of $\Delta E = 2.4$ eV.

The hardness of InN is less than that of AlN and GaN, the density is 6.88 g/cm^3, and the heat of formation from the elements is 4.6 kcal/mole [33]. The energy of dissociation is equal to 70-116 kcal [611].

Chemical properties. According to data of [612], indium nitride is very unstable in a chemical respect. It is rapidly decomposed by sulfuric, nitric and hydrochloric acids and by aqueous solutions of alkalis with boiling (in work [574] of indium nitride is assigned a higher chemical stability). In air it is stable up to a temperature of 300°C and at 350°C almost completely and in a stepwise manner oxidizes to In_2O_3, and oxidation is completely finished at 600°C (Fig. 124).

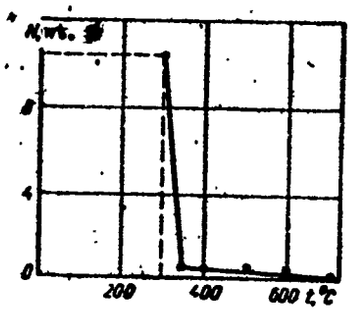

Fig. 124. Kinetics of the oxidation of InN in air.

Methods of production. Indium nitride is usually produced by the decomposition of ammonium hexafluorindate (NH_4InF_6) at 600°C [6, 31, 33, 102]. Later Renner [574] describes the method of producing InN by the decomposition of indium chloride $InCl_{3x} \cdot xNH_3$ at temperatures of the order of 400°C. In that part of the reaction tube which has a temperature of 600°C for several hours a black layer is deposited, and with the very slow process and corresponding temperature rate of indium nitride will be formed in the form of brown transparent crystals.

In work [622] indium nitride is produced by the reaction of indium oxide with ammonia

$In_2O_3 + 2NH_3 = 2InN + 3H_2O$

with the use as a scarifier (for increasing the reaction surface) carbonate ammonium. After 4 hours at a temperature of 610°C with the ratio $In:(NH_4)_2CO_3 = 1:3$, indium nitride of a practically stoichiometrical composition will be formed.

In survey [614] the fundamental possibilities of producing single crystals of indium nitride are discussed.

5. Thallium Nitrides

In certain sources [1, 6] the existence of the nitride TlN, formed at a temperature of 620°C by the reaction of thallium vapors with ammonia [623] is indicated. With heating in hydrogen it is reduced to metallic thallium. The energy of dissociation is equal to 52-92 kcal/mole [611].

Thallium nitride of the composition Tl_3N is produced by the reaction $3TlNO_3 + 3KNH_3 = Tl_3N + 3KNO_3 + 2NH_3$, which leads to the deposit of thallium nitride in the form of a black deposit [624]. The Tl_3N explodes upon contact with water or diluted acids and with heating or a shock. Let us dissolve $TlNO_3$ and KNH_2 in ammonium solutions.

With the reaction of NaN_3 with the solution of thallium sulfate or nitrate, azide TlN_3 will be formed, which is well soluble in hot water. It is necessary to note that in the attempt to reproduce these data positive results were not obtained; thus, the existence of thallium nitrides is very problematical.

Footnotes

[1]According to data of [639], resistance BN at 2000°C is $2 \cdot 10^3$ Ω·cm.

[2]A detailed study of the stability of AlN in mineral acids and solutions of alkalis is conducted in work [612].

C H A P T E R VII

NITRIDES OF ELEMENTS OF THE CARBON SUBGROUP

1. Silicon Nitrides

An investigation of conditions of producing and properties of compounds of silicon with nitrogen, which started as early as 1844, showed the presence in this system of several chemical compounds to which compositions SiN, Si_2N_2, Si_3N_4 are ascribed. At present the existence in the silicon-nitrogen system of only chemical compound - silicon nitride Si_3N_4 is uniquely proven.

One of the first investigations of the structure of this compound was carried out in [525, 1025]. A rhombic structure was set with lattice constants: a = 13.38, b = 8.60, c = 7.74 Å (see also [529, 532]). Then it was reported about the hexagonal silicon nitride [526]. Turkdogan, Bills and Tippet [527], and also authors [526] revealed that there are two modifications of nitride α- and β-Si_3N_4 roentgenographically investigated in [528, 559]. Both modifications proved to be hexagonal.

Both structures are constructed from tetrahedrons SiN_4, and the difference consists in the method of joining these tetrahedrons (tetrahedrons SiN_4 are almost regular, and the distances of Si-N 2.72-1.75 Å).

The structure of β-Si_3N_4 (space group $P6_3/m$) can be removed from

the structure of phenacite Be_2SiO_4 by the substitution of oxygen and beryllium atoms by nitrogen and silicon atoms respectively. Each silicon atom is found in the center of a slightly incorrect tetrahedron of nitrogen atoms. Cells Si_3N_4 are connected by common angles in such a way that each nitrogen atom is common for all tetrahedrons. Otherwise the structure can be represented in the form of eight-member rings Si_3N_4 united with each other in the appropriate way.

The structure of α-Si_3N_4 (space group $P31_c$) is different than the β-modification: in latter the planes are united along the direction (001) in the sequence ABABAB..., whereas in the lattice of α-modification - in the sequence ABCDABCDABCD...

The number of formula units in the unit cell of the α-modification is equal to four, and in the β-modification - two.

The following data for lattice constants are obtained [530, 531]:

Modification	a, Å	c, Å	c/a	Literature
α-Si_3N_4	7.748	5.617	0.725	[528]
	7.76	5.62	0.726	[530]
	7.76	5.64	0.727	[531]
β-Si_3N_4	7.608	2.9107	0.3826	[528]
	7.59	2.90	0.383	[530]
	7.59	2.92	0.335	[531]

The solubility of nitrogen in solid silicon is not quite definitely established, and the solubility in liquid silicon is of the order of 10^{19} atoms/cm^3.

Physical properties. Atoms of silicon and nitrogen in Si_3N_4 are united by covalent saturated bonds, the presence of which follows from the fact that every fourth hybrid sp^3-orbit of the atom is covered with a hybrid sp^2-orbit of a nitrogen atom [528]. The remaining completely occupied p-orbits of each nitrogen atom are perpendicular to three planes of sp^2-orbits and cannot

participate in the bond. The covalence of the bonds is indicated, in particular, by the high electrical resistance of the nitride, which consists of more than 10^{12} Ω·cm [529]. A detailed investigation of the electrical resistance of silicon nitride is carried out in [534], where it is shown that the electrical resistance of Si_3N_4 at room temperature is 10^{13}-10^{14} Ω·cm , and with an increase in temperature it rapidly drops, reaching at 300°C to $2 \cdot 10^8$ Ω·cm (Fig. 125). The sharp bend on the curve of electrical conductivity at 700°C corresponds to modification transformation, also established dilatometrically (Fig. 126). The phase transition displaces impurity level in the energy spectrum Si_3N_4. The value of the energy of activation of impurities E_0 = 1.13 eV at 300-650°C and 3.91 eV at 650-1200°C. In the second case, apparently, chiefly an intrins. conductivity is observed, and quantity E_0 approximately characterizes the width of the forbidden band of silicon nitride. The addition to the carbon nitride decreases and titanium nitride increases the electrical resistance of the nitride (see Fig. 125).

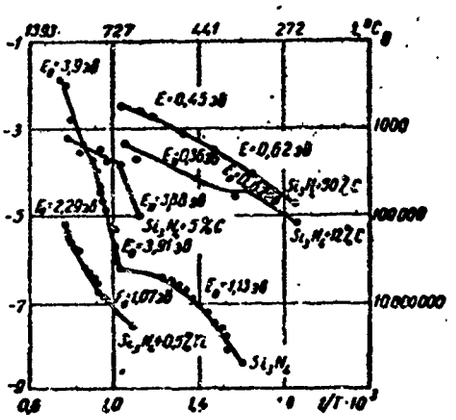

Fig. 125.

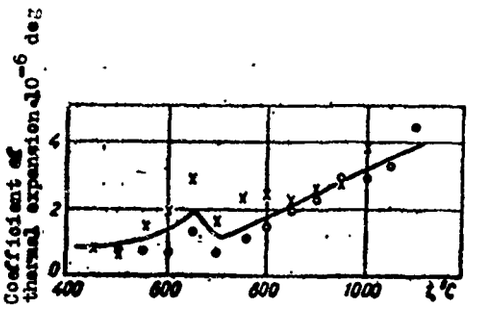

Fig. 126.

Fig. 125. Dependence of electrical conductivity of silicon nitride and alloys of silicon nitride with titanium and carbon on temperature. Designation: эВ = eV.

Fig. 126. Dilatometric curve of silicon nitride.

In accordance with the strong covalent bonds between the atoms, silicon nitride possesses high hardness and small coefficient of

thermal expansion. The energy isolation of groups of atoms entering into its composition causes its dissociation to smelting, just as all other covalent nitrides possessing nonmetallic properties do.

The pressure of dissociation of silicon nitride is expressed by the equation [74]

$$\lg p = -\frac{19250}{T} + 8{,}54.$$

The pressure of dissociation, equal to 1 at, is reached at a temperature of 1977°C (see also [1106-1108]).

Below (Table 101) basic data about properties of silicon nitride are given.

Table 101. Properties of silicon nitride

Characteristic	α-Si_3N_4	β-Si_3N_4
Content of Si, wt. %	60,2	60,2
Crystal structure	Hexagonal	Hexagonal
Lattice constants, Å:		
a	7,76 [531]	7,59 [531]
c	5,64	2,92
c/a	0,727	0,335
Density, g/cm³:		
X-ray	3,184 [527]	3,187 [527]
pyonometric	3,19 [527]	3,21 [530]
Melting point, °C	1900 [535]	
Heat of formation, kcal/mole	179,5 [551, 1118]	
Heat capacity (298-900°K), cal/mole·deg	$16{,}83+23{,}6\cdot10^{-3}T$ [47]	
Thermal conduction, cal/cm·deg·s	0,011 [542], see also [551]	
Coefficient of thermal expansion (20-1000°C), $\times10^6$ deg^{-1}	2,75 [535]	
Entropy (S°_{298}), cal/deg mole	23,0±2,5 [47]	
Specific electrical resistance (20°C), Ω·cm	10^{13}—10^{14} [534]	
Dielectric constant (at 28°C)	9,4 [530]	
Microhardness, kg/mm²	3337±120 [544]	
Rockwell hardness (R_A)	99 [535]	
Elastic modulus, kg/mm²	11600—14500 [535	
Tensile stren. with flexure, kg/mm²:		
20°C	16,0 [542]	
1200°C	14,7 [542]	
Radiation factor (λ = 655 nm)		
800-1600°C	0,77 [340]	

Chemical properties. One of the most important properties of silicon nitride is its especially high chemical stability [530, 535, 542]. The chemical properties are given in Table 102.

Table 102. Reagents to which silicon nitride is resistant.

Reagent	State	Stability
20 % HCl	Boiling	(Not decomposed during >500 h)
65 % HNO_3	Boiling	The same
HNO_3	Smoking	The same
10 % H_2SO_4	At 70°C	The same
77 % H_2SO_4	At 20°C	The same
85 % H_2SO_4	The same	The same
HPO_3	The same	The same
$H_4P_2O_7$	The same	The same
20 % NaOH	The same	The same
Cl_2	At 30-900°C	The same
H_2S	At 1000°C	The same
$H_2SO_4+CuSO_4+$ $+KHSO_4$	Concentrated boiling	The same
$NaNO_3+NaNO_2$	Melt at a temperature 350°C	The same
50 % NaOH	Melt at a temperature 790°C boiling	Stable during 115 h
NaOH	Melt at a temperature of 450°C	Stable during 5 h
48 % HF*	At 70°C	Stable during 3 h
3% HF+10% HNO_3	At 70°C	Stable during 116 h
NaCl+HCl	Melt at 900°C	Stable during 144 h
$NaB(SiO_3)_2+V_2O_5$	At 1100°C	Stable during 4 h
$NaF+ZrF_4$	At 800°C	Stable during 100 h

*See also [547].

Silicon nitride is resistant to the action of oxygen. According to data of [530], with the action of oxygen on powder Si_3N_4 at 1000°C for 3 hours 14.7% of this power is oxidized; at 1300°C – 23.6% and at 1400°C – 49.5%. Silicon nitride is even stabler to the oxidation of air. (According to data of [527], with heating in a current of air 1450°C for 20 hours, the increase in weight is a total of 11.3%.) Compact and dense articles can be used in air up to temperature of 1200°C for a sufficiently prolonged time [536]. In work [547] the stability of silicon nitride is the form of powder at 600-1400°C in air and at 1200°C in water vapors is investigated. It is shown that the oxidation in air starts at 1000°C with the degree of transformation of nitride into oxides of 0.11%, and the

further degree of decomposition increases for each 100°C by 0.2-0.3% up to 1400°C, when the rate of decomposition sharply increases and reaches 1.41%. In water vapors in 1 hour at 1200°C the degree of decomposition is more than 2%. The increase in weight of samples Si_3N_4 after 80 hours at 1200°C is a total of 5 mg/cm^2 while samples of TiB_2 – 10, and of TiC – 42.5 mg/cm^2. An even greater resistance to oxidation in air is possessed at this temperature by silicon carbide on a bond of silicon nitride (increase in weight of 2.5 mg/cm^2).

According to data of [991], silicon nitride in air at 1100-1500°C oxidizes basically with the formation of silica; the addition of NaF promotes the oxidation of silicon nitride to hydroxynitride. In coke filling at 1450-1550°C silicon nitride is decomposed with the formation of hydroxynitride and cubic silicon carbide; the addition of CaF_2 and MgO promote the transition of silicon nitride in a medium carbon monoxide at 1550°C in silicon hydroxynitride.

Chlorine weakly acts on silicon nitride at average temperatures. Thus, at 350-420°C after 2 hours the loss of weight with the treatment of the powder of nitride by chlorine is 0.77-0.95% [530].[1]

Silicon nitride is distinguished by very high stability with respect to melted metals. Table 103 gives data obtained during tests of crucibles of silicon nitride prepared by slip casting [535]. It is indicated that especially silicon nitride is resistant to melted aluminum, the stability in which at 982°C reaches up to 3000 h without any noticeable destruction [537]. These data confirm the high resistance of silicon nitride to the action of aluminum and magnesium is also noted in work [547]. Magnesium acts basically on silicon oxide contained in the nitride with the formation of oxide and silicide of magnesium: $SiO_2 + 4Mg = 2MgO + Mg_2Si$. According to

[1]For chemical properties and methods of analysis of silicon nitride see also [110, 530, 532].

data of work [538], the stability of silicon nitride in melts of chlorides in the process of electrolysis is not high.

Figure 127, according to data of G. A. Yasinskaya [539], shows results of the comparative investigation of the stability of articles from silicon nitride and other fireproof materials with short-term contacting. It is clear that transition metals act stronger on silicon nitride and intransitive metals and nonmetals almost do not act. This rather well agrees with magnitudes of interphase energies with the wetting of melts of silicon nitride [540]. According to data of [541] given in Table 103, silicon nitride practically does not react with mattes and slags of nickel melts, cuprous slags, and melts of sodium and calcium chloride, slowly reacts with copper matte and very weakly with melted basalt and mixtures of sodium and barium chloride.

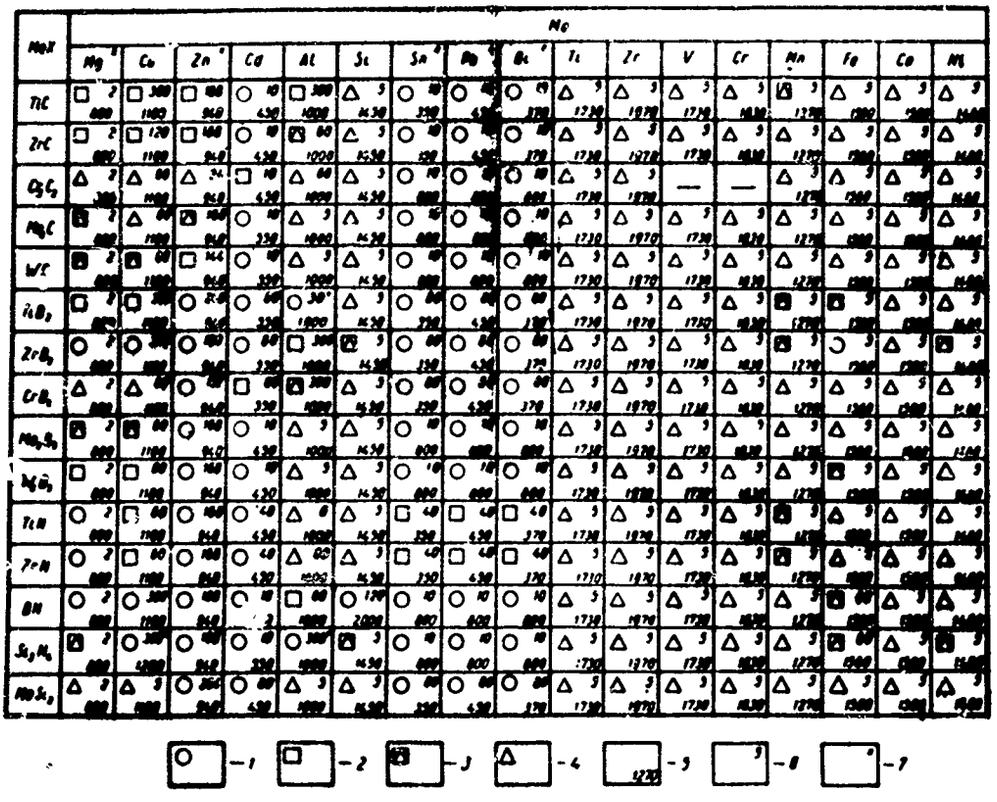

Fig. 127. Character of the reaction of refractory compounds with melted metals: 1 - do not react (1st point); 2 - weakly react (2nd and 3rd point); 3 - react (4th point); 5 - temperature of experiment, °K; 6 - duration of experiment, min; 7 - duration of experiment, h.

Table 103. Resistance of silicon nitride to the action of melts.

Melt	Temperature, °C	Time of contact h	Result of the action on silicon nitride	Literature
Aluminum	800	950	Does not act	[535]
Aluminum	1000	3000	Does not act	[537]
Lead	400	144	Does not act	[535]
Tin	300	144	Does not act	[535]
Zinc	550	[illegible]	Does not act	[535]
Magnesium	75[illegible]	[illegible]	Weakly acts	[535]
Copper	115[illegible]	[illegible]	Strongly acts	[535]
Copper matte	13[illegible]	5	Acts	[541]
Cuprous slag	1300	5	Does not act	[541]
Nickel matte	1250	5	Does not act	[541]
Nickel slag	1250	5	Does not act	[541]
Basalt	1400	?	Weakly acts	[541]
NaCl + $CaCl_2$	700	50	Does not act	[541]
NaCl + $BaCl_2$	1100	3	Weakly acts	[541]

Methods of producing. To produce silicon nitride many methods are known:

1. Direct nitridation of silicon. This method is described for the first time by Balmain [543], who by heating silicon in a medium of nitrogen, which is separated with the decomposition of potassium cyanide, produced silicon nitride of an indefinite composition in the form of the porous fragile sinter.

In [535], for the production of nitride, the heating of silicon in a medium of nitrogen at a temperature of 1300°C was conducted. For nitriding are the most favorable dimensions of powder particles are 150 meshes, in the use of which nitride powder with a coarseness of the particles of 1-10 μm is obtained.

The kinetics of the nitriding of silicon powder (with a purity of 99.2% and maximum coarseness of the particles of 40 μm) was investigated in [544]. The obtained kinetic curves of saturation by silicon nitrogen are shown on Fig. 128. The formation of silicon nitride starts at a temperature of 970°C. Reaction constant of nitriding at this temperature is $7.49 \cdot 10^{-7}$ g/cm^2, at 1490°C - $2.00 \cdot 10^{-4}$ g/cm$^2 \cdot$s. With a further increase in temperature up to 1600°C the constant of the rate of nitriding remains constant, and at higher temperatures it decreases sharply.

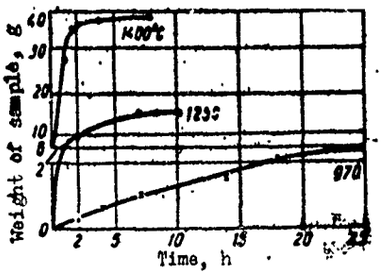

Fig. 128. Kinetic curves of the saturation of silicon by nitrogen.

Thus, nitriding at temperatures above 1600°C causes a decrease in the increase in weight as compared to the increase in weight at a temperature of 1600°C, and temperatures above 1600°C the rate of dissociation prevails over the formation rate of nitride. According to data of this work, the activation energy with the reaction diffusion of nitrogen in silicon is 33,800 ± 7190 cal/mole.

It is necessary to note the volatilization of silicon nitride (suppressed by the high formation rate) is already revealed in the temperature interval of 1200-1400°C [545]. It is assumed that silicon nitride Si_3N_4 dissociates at these temperatures not to silicon and nitrogen, but, in partially losing the nitrogen, passes into the lowest silicon nitrides, for example, Si_2N_3. However, in this work tenseness of such explanation is noted, since lowest silicon nitrides in the system silicon-nitrogen are not revealed.

Somewhat different data on direct silicon nitriding are obtained in [530]. It was determined that nitriding, recorded according to the increase in weight, starts at a temperature of 1230°C, regarding the optimum temperature of the formation of nitride, then the temperature at 1450°C indicated in this work agrees well with the temperature at 1400-1490°C established in [544].

In the same way data about the time necessary for maximum saturation of the silicon by nitrogen at a temperature of 1400°C agree well (at lower temperatures in [530] saturation to limit was not produced).

Authors [526, 547] produced silicon nitride by nitration at temperature of 1200-1600°C. The most thorough study of silicon nitration is conducted in [532], where it is shown that the character of kinetic curves of saturation of silicon by nitrogen is somewhat different in ranges of 1240-1315°C, 1315-1385°C, 1385-1415°C and above 1415°C (Fig. 129). It is assumed that the first of the indicated ranges corresponds to the sample dissolution of nitrogen in silicon (purely diffusion process). Acceleration of the reaction observed in the range of 1315-1385°C can be explained by the distinction of coefficients of thermal expansion of silicon and silicon nitride, which causes stresses in the nitride film, the appearance in it breaks, vacuums, and cracks with the corresponding baring of the surface of silicon and acceleration of the nitriding. A defined role is played by the pressure of crystallization of the silicon nitride produced. At a temperature above 1385°C and up to 1415°C the reaction occurs up to full nitriding of the silicon; its high rate, just as in the preceding stage, is also explained by the cracking of the nitride layer, especially 1415°C, since the melting point of silicon (1412°C) its vapor pressure is high, and the vapors destroy the nitride film, transforming it into microporous body, through which nitrogen easily passes.

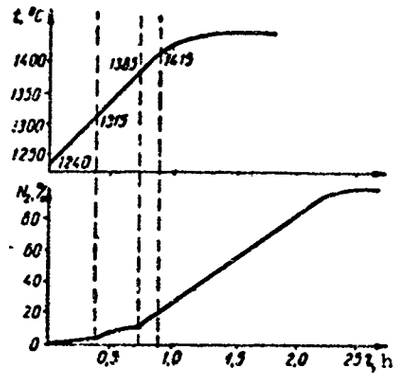

Fig. 129. Kinetic curves of the nitriding of silicon [532].

In work [527] it is shown that the reaction of the formation of silicon nitride with the nitriding of silicon powder accelerated sharply with the addition in the latter of 1% CaF_2, which is a catalyst of this reaction.

The authors [1046] investigated the effect of additions of different metals (an amount of 2 wt. %) on the degree of the transformation of silicon into nitride with nitriding for 5 hours at 1300°C in a current of nitrogen. It was found that the most active catalysts of the process are manganese, iron, cobalt, palladium, nickel, and also copper; much weaker were titanium, vanadium, chromium, molybdenum, and gold, and silver and zinc even prevent the reaction of the nitriding of silicon. Since nitriding is conducted with molecular nitrogen, it is possible to assume that the action of the catalyst consists in the disturbance of the bond between atoms in a molecule of nitrogen, which is possible if the catalyst is an acceptor of the electrons. All metals revealing the catalytical activity with the nitriding of silicon are strong acceptors, which tend to the localization of valence electrons with the formation of maximum statistical weight of the atoms with stable electron configurations. The number of metal-catalysts includes for example, nickel, the acceptor properties of which are so great that is is able to accent the valence electrons of even tungsten; similar strong acceptors are also platinum, palladium, copper and manganese.

The industrial technology of producing silicon nitride is described in [548]. The silicon is crushed pulverized and thoroughly washed of the iron, after which it is nitrided according to two-stage conditions: at 1300-1350° and at 1500-1550°C for 3 hours in each step. Expenditure coefficients (for 1 kg of nitride) are: 1 kg of silicon, 6 m^3 of nitrogen, 70 kW of electric power; the obtained technical products contain 58-59% $Si_{общ}$, up to 20 $Si_{своб}$ and 35-38% of nitrogen.

Direct nitriding of silicon can also be conducted with ammonia [532]. In [531] by the same method silicon nitride was produced by the action on powdery silicon of ammonia at 1200-1500°C, in [559] α-Si_3N_4 was produced at 1350-1450°C and β-Si_3N_4 at 1500°C for 3 days.

2. Heating of the mixture of silica and carbon in a medium of nitrogen. The reaction $3SiO_2 + 6C + 2N_2 = Si_3N_4 + 6CO$, results of the investigation [544] showed, at a temperature of 1000-1800°C passes not in the direction of the formation of silicon nitride but silicon carbide, the content of which is products of the reaction is increased from 15% at a temperature of 1400°C to 85% at 1800°C; the nitride content at all temperatures does not exceed 2-4%.

Therefore, Weiss and Engel'gardt [549] investigated the effect of additions in the charge directing the reaction in the direction of the formation of nitride and accelerating it. They revealed that with the addition of the charge of 10% iron oxide the reaction at a temperature of 1250-1300°C passes with the preferential formation of silicon nitride, which is washed of compounds of iron by hydrochloric acid.

3. Other methods of producing silicon nitride. Schutzenberger and Kelson [550] produced silicon nitride, to which they ascribed the composition Si_2N_3, by the action of nitrogen on silicon carbazote C_2Si_2N at high temperatures. There is pointed out the formation of silicon nitride of the composition SiN_2 by heating of triimidodisilane at a temperature of 400°C [551]. The producing of silicon nitride is described by the nitriding of $CaSi_2$ with subsequent washing of the product of reaction by hydrochloric acid [552].

The authors [530] produced silicon nitride of α-modification by heating the compound $Si(NH)_2$ at 1350°C; a similar method was proposed earlier by Blix and Birnbauer [553] and in [554].

Billy [532] investigated reactions of the interaction tetrachloride and tetrabromide of silicon with ammonia, showed that in this case there will be formed not silicon nitride, but, for example, silicon imide SiN_2H_2 or ammonia bromide of ammonium ($NH_4Br \cdot xNH_3$).

In work [527] silicon nitrides were produced by the nitriding of

silicon iron alloys, which contain from 2.83% Si with the subsequent separation of nitride by the treatment brommetyl ester of acetic acid. An X-ray investigation showed the presence of only α-Si_3N_4. After that the nitriding of different alloys of iron, nickel, manganese with silicon was conducted, and it is shown that in the composition of the alloy silicon nitride has a structure different from α- from β-Si_3N_4, but, being separated from the alloy by chemical means, it is always turned into α-Si_3N_4. It is assumed that this is caused by the formation in alloys of complex nitrides $Me_xSi_yN_z$, which with chemical treatment are decomposed with the separation of Si_3N_4. Conversely, in [560], where distinction of structure of silicon nitride in silicon iron alloys from the structure Si_3N_4 was also noticed, it was assumed that in the alloys there will be formed the lowest silicon nitrides, which, in general, is improbable, although their existence is indicated in early works. In presence of iron silicon nitride is decomposed with the separation of nitrogen [530].

The question about the behavior of nitrogen is silicon iron alloys, in particular, in transformer steels, is also discussed in [561-563].

Thus, just as was indicated above, the only real method of producing silicon nitride is the direct nitriding of silicon by nitrogen or ammonia.

Producing articles from silicon nitride. The most technological method of producing articles from silicon nitride is the so-called reaction sintering, which consists in the nitriding of billets pressed from silicon where processes of the formation of silicon nitride and its sintering are combined. This process was first studied in work [535, 558], where billets from silicon powder, formed by the method of slip casting, were subjected to treatment by nitrogen. Nitride produced in the nitriding of each particle fills the volume of the pores, since the specific volume of nitride substantially exceeds the specific volume of the initial silicon,

in practice in this case slightly porous or, in general, nonporous articles can be produced. For the same reasons, i.e., due to the fact that an increase in volume with nitriding is realized as a result of the filling of the pores, the change in overall dimensions of the billets with reaction sintering is small; for example, according to data of [535], it does not exceed ±0.005 mm/mm; in [542] no change in the dimensions was also observed.

Reaction sintering of silicon nitride is investigated also in [557, 234]. It is indicated that for the approach to the producing of articles of theoretical density, it is necessary to use billets from silicon having the largest possible density (80-85%), which, however, is practically difficult in connection with the poor compactibility of the silicon powder.

The technological layout of this method of producing articles is described in detail in [548].

To produce large-dimension articles from silicon nitride, it is usually more convenient to use the method of pressing of billets from nitride powder with subsequent sintering in a medium of nitrogen [548, 555]. Although the nitride powder is pressed better than silicon powder, for the pressing of billets use different plasticizer-glues in particular, 5% solution of rubber in gasoline, 5% aqueous solution of polyvinyl alcohol, or starch paste (chiefly the first two, since with the burning out of the starch paste many ashes remain). Pressing is conducted under a pressure of 1-2 t/cm^2 (residual porosity of the billets is about 30%), the pressed billets are dried, baked in a medium of nitrogen, at first 500-600°C for removal (burning out) of the plasticizer and then 1550-1600°C for 2-3 hours. In the use of powder of silicon nitride with a high content of free silicon one more temperature step is introduced, 1350°C for the nitriding of silicon. With sintering, shrinkage of the articles is absent and the porosity is not changed, i.e., it remains practically the same as that in pressed billets.

It is convenient to produce initial billets, especially for producing complex shaped articles, by slip casting [555, 556], in gypsum molds with the use of drosses prepared on 1-1.5% solution of polyvinyl alcohol (Ж:Т = 40:60, pH = 5, electrolyte – HCl).

In work [564] it is proposed to obtain dense articles from silicon nitride by the method of hot pressing with so-called fluxing additions, from which the best result is given by MgO and Mg_3N_2, with the introduction of them into silicon powder in the amount of 0.1 to 10% (usually – 5%). Hot pressing is carried out in graphite molds under a pressure of 210 kg/cm^2 and at a temperature of 1600-1900°C (usually 1850°C). The open porosity of the obtained articles does not exceed 20% and basically reaches to 0.5%, and the bending strength is 35-84 kg/mm^2 at 20°C and 14-42 kg/mm^2 at 1200°C. The loss in weight with heating in air at 1100°C consists of less than 1 mg/cm^2.

Thus, with hot pressing it is required to introduce into the composition of nitride additions, and the pure silicon nitride is poorly baked by hot pressing. In work [542], for the production of dense compact articles from nitride, hot pressing of its mixtures with silicon (with the content of silicon in the mixture at more than 20%) is proposed, which at a temperature of 1400°C and pressure of 800 kg/cm^2 leads to the producing after additional nitriding of articles with a rather high density (this process is similar to the producing of self-bonded silicon carbide). A study in this work of the effect of the temperature of nitriding on the strength of the silicon nitride showed that the highest lending strength is possessed by samples produced by nitriding at 1600°C ($\sigma_{изг}$ = 16 kg/mm^2).

Without hot pressing by separate pressing and sintering, relatively dense articles can be obtained from silicon nitride with magnesium oxide or with aluminum oxide, which are resistant to oxidation at 1200°C and possess high fireproof properties, especially in melted borax, zinc and so forth.

At present attempts are being made to produce fibers from silicon nitride [557].

Conditions of formation and certain properties of pyrolytic silicon nitride [1006] in the form of thin films are also investigated. The density of pyronitride is equal to 3.02-3.21 g/cm^3, the refractive index is 2.0-2.06, the dielectric strength is 10^7 V/cm, and its chemical stability in different reagents is very high. Thus, the corrosion rate in 48% HF is a total of 75-100 Å/minutes.

Articles from silicon nitride yield well to the action of the usual methods of machining (they are similar to in this respect to elephant bone), and they are very easily treated by ultrasonics [776].

An external view of articles from silicon nitride which are basically of fireproof assignment, is shown on Fig. 130.

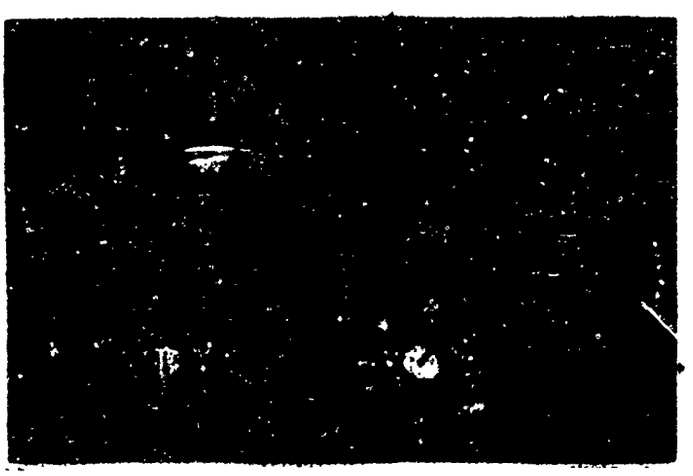

Fig. 130. External view of articles from silicon nitride.

2. Germanium Nitrides

In the Ge-N system by different investigations the compounds Ge_3N_2 and Ge_3N_4 are found [6, 525, 565-567]. However results of a

recently performed work [568] showed that the nitride Ge_3N_2, apparently, does not exist. Consequently, germanium will form one nitride with nitrogen – Ge_3N_4.

The structure of Ge_3N_4 was investigated by Juza and Hahm [102], who revealed that this compound is isomorphic to phenacite Be_2SiO_4, and has a hexagonal lattice with parameters a = 13.84, c = 9.25 Å and c/a = 0.668. Subsequently the structure of this compound was investigated repeatedly, so that in [525] for it the rhombic lattice with parameters a = 13.38, b = 8.60 and c = 7.74 Å was shown; in [529] two modifications are revealed – α-Ge_3N_4 with a rhombic lattice (a = 4.10, b = 7.10, c = 5.94 Å) and β-Ge_3N_4 with a rhombohedral (a = 8.62, α = 108°). Here it was established that α-Ge_3N_4 will be formed with the treatment of germanium by ammonia and β-Ge_3N_4 – with the reaction of GeO_2 with ammonia.

It is necessary to consider that both crystal modifications of germanium nitride are hexagonal and isostructural to the corresponding modifications of silicon nitride.

Physical and chemical properties. Nitride Ge_3N_4 a light-brown substance with reddish shade possesses high electrical resistance (of the order of 10^8 Ω·cm [33]), density of 5.29-5.31 g/cm^3 [33, 102]. At a temperature of more than 850°C germanium nitride is completely decomposed into elements (up to 850°C in a medium of nitrogen, it is stable). Heat of the formation is 15.6 + 1.7 kcal/mole [569].

However, in [1060] this value is substantially corrected and is from 90 ± 8 to 94 ± 3 kcal/mole. The evaporation of germanium investigated in the same work in the temperature range of 923-963°K by the effusion method of Knudsen showed that with evaporation this nitride dissociates to hard germanium and nitrogen. The pressure of nitrogen above the germanium nitride is $2.40 \cdot 10^{-2}$ at at 933°K increasing at 963°K to $4.27 \cdot 10^{-2}$ at.

Germanium nitride starts to be oxidized in air at 750-800°C,

and oxidation is completely finished at 950°C (with the transformation of GeO_2).

Methods of producing. Germanium nitride Ge_3N_4 can be produced by different methods [568], the most widespread of which is the treatment of germanium by ammonia. As can be seen from Fig. 131 (curve 2), nitriding starts at 700°C and especially actively terminates at 750°C. However, even at 800°C germanium nitride of stoichiometric composition will not be formed and a further increase in temperature causes decomposition of the product already formed. For the development of the surface of nitration, in work [568] it was proposed to mix the powder of germanium with a scarifier, which was ammonium carbonate. During the use of a charge from germanium powder and ammonium carbonate in the ratio of 1:2, nitration at 750°C in the course of 1 hour permits producing germanium nitride of practically accurate stoichiometric composition (Fig. 131, curve 3).

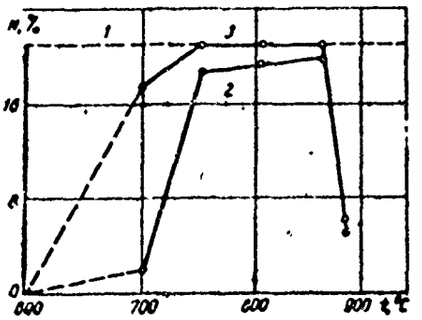

Fig. 131. Results of germanium nitriding: 1 – calculated composition of Ge_3N_4; 2 – treatment of germanium by ammonia; 3 – the same with a scarifier $(NH_4)_2)CO_3$.

It is also possible to obtain germanium nitride by the reaction between germanium and ammonia dioxide in the presence of ammonium carbonate and without it in a current of ammonia. An application of ammonium as a scarifier permits lowering the temperature of nitriding down to 750°C. Without the scarifier the reaction is completed in 4 hours at 800°C, and at 850°C the time of nitriding is reduced to 1 hour, but technologically this temperature is dangerous, since its small excess leads to the decomposition of the nitride.

In work [569] α-Ge_3N_4 was produced by the action of ammonia on the germanium powder and β-Ge_3N_4 – on GeO_2 at 750°C.

Nitrogen does not act on germanium.

3. Nitrides of Tin and Lead

A report is given about the producing of tin nitride with the probable formula Sn_3N_4 by means of the evaporation of tin in a medium of nitrigen [570, 29]. The solubility of nitrogen is lead up to 600°C is not revealed. Information about the formation of nitrides by it is not available [29].

C H A P T E R VIII

NITRIDES OF ELEMENTS OF THE SUBGROUP OF NITROGEN AND OTHER ELEMENTS

1. Compounds of Phosphorus with Nitrogen (Phosphorus Nitrides)

In the system P-N the existence of compounds P_2N_5, P_3N_5 and PN is established. The most widespread method of producing phosphide P_3N_5 is the reaction of the interaction of sulfide P_4N_{10} with gaseous ammonia with heating [720]. By the thermal decomposition of $P_3N_5 \cdot 7NH_3$ in a current of hydrogen [721] or by heating of $PNCl_2$ in a current of ammonia up to 825°C [722] it is difficult to produce phosphide P_3N_5 of an exact composition.

Phosphide PN is obtained by the thermal decomposition of P_3N_5 in the range of 750-810°C.

The authors [723] investigated the equilibrium between the PN vapor and the equimolar mixture of phosphorus and nitrogen at 900°C, the rate of decomposition of the PN vapor and the kinetics of the synthesis of phosphorus nitrides from elements (on an incandescent tungsten thread). The equilibriums $(PN)_{x,тв} \rightleftarrows xPN_{газ}$ and $2PN_{газ} \rightleftarrows P_{2,газ} + N_{2,газ}$ were examined taking into account the equilibrium $P_{4,газ} \rightleftarrows 2P_{2,газ}$.

It was determined that the equilibrium concentration of phosphorus at 900°C is 1-3 vol. % at 0.7-1 at, which leads to the value of the energy of dissociation D for PN equal to 7.1 ± 0.05 eV. For

the equilibrium constant of the synthesis of PN, from the elements values from $1 \cdot 10^{-2}$ at 900°C to $2 \cdot 10^{-1}$ at 2000°C are obtained. The mean value of the heat of formation of the PN from elements according to the reaction $P_{2,газ} + N_{2,газ} = 2PN_{газ}$ is 14.2 kcal/mole. The activation energy of the given reaction is equal to 31 kcal/mole, and this value shows that synthesis reaction of PN passes not through the stage of free atoms P and N. The formation rate of solid PN from P_2 and N_2 on tungsten thread at 1720-2127°C is proportional to the square root of the concentration of phosphorus. The activation energy at a temperature above 1800°C is equal to 59 kcal/mole, which is close to the energy of dissociation of phosphorus on the atoms. The ratio N:P in solid products of condensation was changed from 1.03 to 1.19 (in the initial gas mixture this ratio was 1). This deviation is explained by the formation on the surface of tungsten of complexes from P atoms and N_2 molecules of the type PNN, which react then with P or N atoms with the formation of polymers up to the composition $(P_3N_5)_x$.

The PN phosphide can also be produced with thermal decomposition P_3N_5 in the range of 750-810°C.

With the transmission of the current of nitrogen with phosphorus vapors through the electrical arc amorphous phosphorus nitrides are obtained with the ratio N:P in the range 1-1.5. With the heating of them to 800-900°C in a current of ammonia this ratio increases to 1.7, i.e., nitride P_3N_5 having a crystal structure will be formed [724].[1]

At room temperature phosphorus nitrides are completely inert, cold water does not act on them and hot water reacts slowly, and they are not decomposed upon heating in concentrated and diluted HCl, diluted HNO_3 and alkalis solutions. They are determined

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[1]For the X-ray analysis of phosphorus nitrides see [725].

insignificantly with prolonged boiling in concentrated HNO_3 and diluted H_2SO_4. Chlorine does not act on them [726].

Upon heating to 500-700°C the phosphorus nitrides start to act as strong reducers due to the decomposition into nitrogen and elementary phosphorus [724].

The density of P_3N_5 is equal to 2.57-2.58 g/cm^3 [720], and the heat capacity up to 300°C is expressed as $C_p = 5.20 + 102 \cdot 10^{-3} T$ [84].

In practice in the majority of the methods of producing phosphorus nitrides of inconstant composition and in amorphous form will be formed; the transfer of them in compounds of defined composition is produced with heating in defined conditions.

2. Compounds of Arsenic, Antimony and Bismuth with Nitrogen

There is no reliable information on the direct compounds As, Sb and Bi with nitrogen.

3. Compounds of Elements of the Subgroup of Oxygen with Nitrogen

Compounds of oxygen with nitrogen. Nitrogen with oxygen will form these oxides: oxide N_2O, nitrogen oxide (monooxide) NO, nitrogen trioxide N_2O_3, nitrogen dioxide NO_2, nitrogen tetroxide N_2O_4 and nitrogen pentoxide N_2O_5, the methods of producing which and the physicochemical properties are described in detail in courses of inorganic chemistry [727]. All these compounds have a covalent character of the bonds.

Nitrous oxide N_2O is a colorless gas with the boiling point of 89.5°C, melting point of 102.4°C, critical temperature of 36.5°C, and critical pressure of 71.1 at. The structure of the solid nitrous oxide is cubic (isomorphic CO_2) with the most compact cubic

packing of molecules N_2O, and linear CO_2 molecules are directed along four nonintersecting axes. The lattice constants a = 5.656 Å. Langmuir proposed for N_2O the following electron structure: $\ddot{N}::N::\ddot{O}$, which was then augmented by resonance forms: $\dot{\ddot{N}}^-::N^+::\ddot{O}$ and $:N^+::\dot{N}:\ddot{O}^-:$.

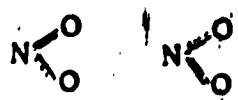
In accordance with this structure the molecule of N_2O has a very small dipole moment equal to $0.14 \cdot 10^{-18}$ esu. From the point of view of the formation of states with a minimum of free energy it is possible to represent the molecule of N_2O as a result of the transformation of the configuration of nitrogen atoms s^2p^3 in sp^3 and transferring of mobile electrons to the atom of oxygen with the formation of the configuration of s^2p^6. Thus, in the molecule of N_2O one should expect a high statistical weight of sp^3-configurations of nitrogen atoms and s^2p^6-configurations of oxygen atoms, which are connected with each other by exchange through part of the electrons which remained nonlocalized in these configurations. Such a structure satisfactorily explains the fact that, in spite of the metastability, nitrous oxide starts to be decomposed at relatively high temperatures.

Nitrogen monooxide NO is a colorless gas with a boiling point of 151.8°C and melting point of 163°C. In accordance with concepts of Pauling, in NO a typical three-electron bond is carried out: $:\dot{N}::\ddot{O}:$ with the appropriate resonance forms [727]. The imposition of the three-electron bond on the usual homepolar bond formed by electron pairs somewhat reinforces the bond of nitrogen with oxygen. This reinforcement is small, since the dimerization of NO molecules in N_2O_2 with the coupling of unpaired electrons takes place only in a liquid and not in a gaseous state where NO monomolecules exist. The presence of the three-electron bond conditions paramagnetic quality of the nitrogen monooxide. The dipole moment of NO is equal to $0.6 \cdot 10^{-18}$ esu. In a liquid state is is completely polymerized, which causes its high heat capacity, which is greatly dependent on temperature, and high entropy of evaporation.

Just as in the preceding case, it is possible to assume that in nitrogen oxide atoms of nitrogen and oxygen will form sp^3- and s^2p^6-configurations and will form them alternately; these configurations are bound by electrons found in the state of exchange between them. Such a type of bond can conditionally be called running.

Nitrogen trioxide N_2O_3, with a melting point of 102°C is easily decomposed into NO and NO_2 or into No and N_2O_4. The heat of formation of N_2O_3 from NO and NO_2 is only 9.6 kcal/mole, and the free energy of the formation is equal to 0.44 kcal/mole.

Nitrogen dioxide NO_2 and nitrogen tetroxide $N_2O_4 \cdot NO_2$ are a brown gas with a boiling point of 22.4°C and melting point of 10.2°C. Upon cooling NO_2 is dimerized passing into a colorless $N_2O_4 \cdot NO_2$, is paramagnetic, and N_2O_4 is diamagnetic. The diamagnetism of the latter explains the tendency of NO_2 to dimerization with the pairing of unpaired electrons. According to Pauling, in the molecule of NO_2 there takes place the imposition of the three-electron coupling on the usual paired electron with mesomerism of the two states



The conductivity of the liquid N_2O_4 at 17°C is equal to $1.3 \cdot 10^{-12}$ $\Omega^{-1} \cdot cm^{-1}$, the dielectric constant is 2.42, the index of refraction is 1.420, at 20°C the molar refraction is 15.2 cm^3, and the molar polarization is 26.5 cm^3. In a solid state N_2O_4 has a cubic lattice with a = 7.77 Å.

Nitrogen pentoxide N_2O_5 will form colorless solid crystals of hexagonal syngony, a = 5.410; c = 6.570 (at 80°C), the specific gravity is 1.63 g/cm^3, the melting point is 30°C, the boiling point is 45-50°C and in a solid state is has salt-like structure built from triangular ions $(NO_3)^-$ and linear ions $(NO_2)^+$.

There are data on the existence of nitrogen oxide NO_3 even richer in oxygen a very unstable compound, which is formed with the reaction NO_2 or N_2O_5 with ozone.

Compounds of sulfur with nitrogen. Sulfur will form two compounds with nitrogen - [727, 728] - sulfur nitirde S_4N_4 and nitrogen tetrasulfide S_4N_2.

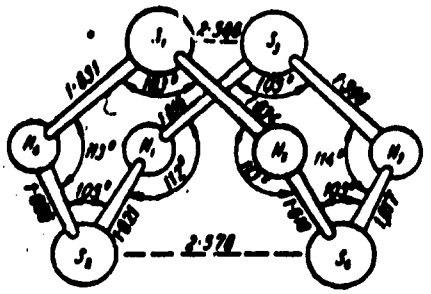
Sulfur nitride is produced by the interaction of sulfur with liquid ammonia

$$10S + 16NH_3 \rightarrow 6(NH_4)_2S + S_4N_4.$$

The structure of this compound, according to data of [729], is shown on Fig. 132 (see also 730). Figure 133 shows the possible resonance forms of the electron structure of nitride S_4N_4 [720]. It constitutes golden-yellow crystals with a melting point of 178°C, the compound is greatly endothermic (with the formation from elements 128 kcal/mole is absorbed), and therefore upon heating or detonation it disintegrates with an explosion. It will somewhat dissolve in organic solvents, is hydrolyzed by water with prolonged boiling with the formation of ammonia and oxyacids, and with sublimation in a vacuum is depolymerized with the formation of S_2N_2 - a crystalline substance stable only at low temperatures, and at room temperature is slowly transformed into the mixture of S_4N_4 and a high polymer compound $(SN)_x$. The last compound is stabler than S_2N_2 and S_4N_4 and possesses semimetallic conductivity.

Nitrogen tetrasulfide is a crystalline substance of dark-red color with a melting point of 23°C and density of 1.71 g/cm^3, and it is produced by the action of carbon bisulfide on sulfur nitride at 100°C under pressure or with the decomposition of the sulfur nitride. It is decomposed at the usual temperature and flashes upon heating and it is dissolved by many organic solvents and by water is gradually decomposed with the separation of sulfur and ammonia. It is assumed that this compound has a cyclical structure with the

content in the S_4N_2 molecule of ions S^{4+} and S^{2+} of two neutral S atoms with negative nitrogen ions [727].



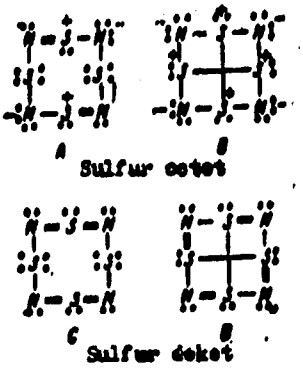


Fig. 132. Fig. 133.

Fig. 132. Diagram of the structure of compound S_4N_4.

Fig. 133. Possible resonance forms of the structure S_4N_4.

[Translator's note: deket could not be found but must refer to the number ten].

Compounds of selenium with nitrogen. Selenium will form with nitrogen the compound Se_4N_4, an orange-red substance with a triclinic lattice and parameters: a = 6.47; b = 6.85; c = 6.35 Å, $\alpha = 99.5°$, $\beta = 100.4°$, $\gamma = 100.4°$ [731].

According to the last data [965], this compound pertains to the space group C 2/c with lattice constants a = 9.65, b = 9.73, c = 6.47 Å, $\beta = 104.9°$.

Its density is 4.2 g/cm^3, and the heat of formation from the elements is 42.6 kcal/mole. It is easily decomposed with a shock or heating to 200-230°C with the separation of selenium. It is insoluble in cold water, and it is slowly decomposed by water upon boiling with the formation of H_2SeO_3, selenium and ammonia. Selenium nitride is produced according to the reaction

$$12SeCl_4 + 64NH_3 = 3N_4Se_4 + 48NH_4Cl + 2N_2,$$

and also by the decomposition of $Se(NH)_2$, the action of dry ammonia on the solution Se_2Cl_2 in carbon bisulfide, and the interaction of benzene with dry ammonia in the presence of $SeO(OC_2H_5)_2$.

The polymer $(NSe)_x$ with a monoclinic lattice with the following parameters is also known: a = 9.65, b = 9.73, c = 6.47 Å, β = = 104.9°.

It was assumed that $(NSe)_x$ consists of four molecules Se_4N_4. However, in [732] it was shown that the most satisfactory correspondence of X-ray density (4.22 g/cm^3), pycnometric (4.2 g/cm^3), is obtained with the acceptance of dimers, i.e., $(NSe)_8$.

Compounds of tellurium with nitrogen [1027]. Two tellurium nitrides are known: TeN (9.89 wt. % N) and Te_3N_4 (12.76 wt. % N). They are obtained by the interaction of tellurium tetrabromide with ammonia

$$3TeBr_4 + 16NH_3 = Te_3N_4 + 12NH_4Br.$$

4. Compounds of Halogens with Nitrogen [727]

Halogens with nitrogen will form two classes of compounds - of the general formula XN_3 (derivatives of hydrazoic acid) and NX_3 (products of the substitution of hydrogen of ammonia by a halogen). Compounds of the first of these classes have the name azides. These azides are well-known: azides of fluorine (FN_3 - yellow-green gas, melting point, 154°C, boiling point, 82°C, explosive in a liquid state), azides of chlorine (ClN_3 - colorless, highly exploding gas), azides of bromine (BrN_3 - liquid), iodine (JN_3 - yellowish-white solid explosive).

Compounds of the second class are nitrogen fluoride NF_3 (colorless gas, boiling point, 129°C, melting point, 208.5°C, density at the boiling point, 1.885 g/cm^3, stable exothermic compound), nitrogen chloride (NCl_3 - dark-yellow volatile oily liquid, specific gravity, 1.65 g/cm^3, highly endothermic, heat of formation, 54.7 kcal/mole, explodes upon heating to 93°C upon contact with substances able to be chlorinated) nitrogen iodide (NJ_3 - a black solid at the usual temperature and highly exothermic).

CHAPTER IX

COMPLEX NITRIDES

At the present time considerable experimental material has been on multicomponent systems, containing nitrogen, in particular on systems, in which ternary and quaternary nitride phases will be formed. It is not possible to expound in detail and to systematize these materials in the present monograph, and also considering that they are to a certain extent expounded in [29, 933], only data about basic and typical systems are presented, in which complex carbide phases, being of scientific and practical interest, will be formed. These data are grouped according to systems, which are formed by different metals with nitrogen ($Me_1 - Me_2 - N$), by metals with boron and nitrogen (boron-nitrides $Me - B - N$), with carbon and nitrogen (carbonitrides $Me - C - N$), with oxygen and nitrogen (oxynitrides $Me - O - N$), with halogens (halonitrides $Me - F - N$, where F is a halogen), with silicon and nitrogen (silicon nitrides $Me - Si - N$), and also by nonmetals with nitrogen ($X_1 - X_2 - N$, where X is a nonmetal). Such a classification naturally does not have special scientific bases and is intended only for ordering the voluminous and disconnected information available in literature about complex nitrides and systems, in which they will be formed.

1. Metal Systems with Nitrogen

Lithium - aluminum (gallium) - nitrogen [426]. The Li_3AlN_2 is obtained by heating lithium with aluminum in a stream of nitrogen at a temperature of 730°C or by heating Li_3Al in a stream of nitrogen

or by heating mixtures of lithium and aluminum nitrides. It is white to light-gray in color; it is stable up to 1000°C, in a nitrogen medium; its density is 2.33 g/cm^3. It hydrolyzes readily; it can join two moles of ammonia. The Li_3GaN_2 is produced by Li_3Ga and nitrogen at 600°C; it is light-gray in color; thermally stable up to ∿800°C; its density is 3.35 g/cm^3. It readily hydrolyzes with the formation of ammonia and nitrogen. In a stream of NH_3 and H_2 it decomposes at ∿400°C. It was determined roentgenographically that both compounds have a superlattice with a CaF_2 lattice, a space group of T^7_h, and 16 formula units in the unit cell. They have the following structural principle: dense packing of the nitrogen atoms with the metal atoms, located in the tetrahedral vacancies of this packing. They possess considerably smaller volumes of unit cells as compared to Li_3N due to the replacement of the single-charge lithium cation by the multicharge cation. Analogous phases are formed by lithium with zirconium and thorium.

Lithium - magnesium (zinc) - nitrogen [911]. In these systems the compounds LiMgN and LiZnN have been detected. The nitride LiMgN is obtained by heating of lithium and magnesium nitrides together in a stream of nitrogen at a temperature of 1050°C. The powder is reddish-brown in color; its density is 2.41 g/cm^3; it hydrolyzes readily; it can join 1 mole of ammonia. The CaF_2 lattice with nitrogen in the positions of the calcium atoms and a statistical distribution of lithium and magnesium in the position of the fluorine atoms is; a = 4.970 Å. The nitride LiZnN is prepared by sintering a mixture of lithium and zinc nitrides at 400°C in a stream of ammonia. It is black; its density is 4.61 g/cm^3; it hydrolyzes readily. The structure is derived from the CaF_2 structure; lithium and zinc are statistically arranged in the fluorine positions; a = 4.87$_7$ Å.

Lithium - Vanadium (niobium, tantalum) - nitrogen [917]. Upon heating Li_3N and VN in a nitrogen medium at a temperature of 680°C the compound Li_7VN_4 will be formed, which more heat resistant than both the original nitrides. It crystallizes into a fluorspar superlattice with a = 9.60 Å. Analogous compounds will be formed

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by niobium and tantalum: Li_7NbN_4 and Li_7TaN_4 - they are chemically and thermally more stable than the ternary nitride of vanadium.

Lithium - vanadium (manganese) - nitrogen [436]. In these systems there were detected the ternary nitrides Li_7VN_4 and Li_7MnN_4, which crystallize in fluorspar superlattice with a doubled lattice constant (the space group is T_0^4). The metal ions in the CaF_2 lattice occupy the fluorine positions. The indicated phases have these respective lattice constants: $a = 9.60_4$ and $a = 9.57_1$ Å and the calculated density values are 2.33 and 2.42 g/cm^3.

Lithium - chromium (molybdenum, tungsten) - nitrogen [912]. By heating mixtures of lithium nitride with chromium, molybdenum or tungsten in a nitrogen medium at a temperature of 616-856°C the ternary nitrides Li_9CrN_5, Li_9MoN_5 and Li_9WN_5 were obtained. Ternary chromium nitride is dark-brown in color; it hydrolyzes in air with the liberation of ammonia, but upon remaining for a long time in air it turns yellow due to the formation of chromate. The nitride has mainly a salt-like character. Since the nitride Li_9CrN_5 forms a continuous number of solid solutions with Li_2O, then it is possible to assume that it is crystallized to a fluorspar superlattice.

Ternary molybdenum nitride is brown in color, but with a lighter tinge than ternary chromium nitride, and ternary tungsten nitride is even lighter, almost gray, Both nitrides decompose with the liberation of ammonia; they dissolve in dilute acids; ternary tungsten nitride is the most heat-resistant of all the nitrides (at 870°C the pressure of nitrogen on it is a total of 3 mm Hg), and the most unstable is chromium nitride. The crystal structure of the ternary nitrides of molybdenum and tungsten is obscure; it is assumed that they each have two versions.

Lithium - cobalt (nickel, copper) - nitrogen [918]. In these systems the component nitrides form the solid solutions $(Li, Co)_3N$, $(Li, Ni)_3N$, $(Li, Cu)_3N$.

Magnesium - germanium - nitrogen [1061]. By the action of ammonia on magnesium germanide the following compound will be formed $MgGeN_2$: $3Mg_2Ge + 8NH_3 = 3MgGeN_2 + Mg_3N_2 + 12H_2$.

This compound can also be produced by the action of ammonia on a mixture of magnesium nitride and germanium: $Mg_3N_2 + 3Ge + 4NH_3 = 3MgGeN_2 + 6H_2$, or by interacting magnesium and germanium nitrides at 850-950°C: $Mg_3N_2 + Ge_3N_4 = 3MgGeN_2$.

The compound is a gray-color powder; it is stable in the presence of water or alkaline solutions; HCl acts on it. It crystallizes into a rhombic system (the space group is C_{2v}^9); the lattice parameters are: a = 5.504; b = 6.660; c = 5.172 Å. Upon heating in argon at 750°C it decomposes into magnesium germanide, germanium and nitrogen, and at 950°C it completely dissociates into its elements. Oxidation begins at 575°C and completely terminates at 950°C. The oxidation products are MgO and $MgGeO_3$.

Strontium (barium) - rhenium (osminum) - nitrogen [994]. Upon heating barium and strontium nitrides with rhenium in nitrogen the ternary nitride phases $Sr_9Re_3N_{10}$, $Ba_9Re_3N_{10}$, $Ba_9Os_3N_{10}$, will be formed, having a rhombic structure, and metallic conductivity; a measurement of the magnetic properties showed the strong interaction of transition-metal atoms in these phases. The phase $Sr_{27}Re_5N_{28}$ also exists - a cubic NaCl type.

Aluminum - gallium - nitrogen. Proceeding from the similarity of crystal structure and the lattice dimensions, AlN and GaN should form a continuous number of solid solutions, however attempts to prepare solid solutions of (Ga, Al)N did not give positive results [599].

The heating of mixtures of these nitrides at a temperature of 900°C for a week in a nitrogen medium did not lead to the formation of a solid solution, but at 1100°C the mixtures exploded due to the high vapor pressure of GaN.

Vanadium (titanium) - chromium - nitrogen. By acting a mixture of ammonia and hydrogen at temperatures of 800-1000°C on precipitates of chromium and titanium hydrates solid solutions of vanadium and chromium or titanium and chromium will be formed nitrides [1024]; in an analogous way ternary solid solutions of titanium - vanadium - chromium nitrides are obtained. All the indicated solid solutions have a cubic face-centered lattice. The thermodynamic stability of CrN and VN increases upon the formation by them of solid solutions of each other or by each of them in titanium nitride [1044].

Titanium - aluminum - nitrogen. In work [418] a compound of the composition Ti_2AlN was detected (it is obtained by the hot pressing of a mixture of TiN, metallic titanium and aluminum). It is isomorphic to Cr_2AlC and Ti_2AlC and has a lattice constant of: $a = 2.99_4$; $c = 13.61$ Å; $c/a = 4.54_4$. The X-ray density is 4.30 g/cm^3.

Titanium - chromium - nitrogen. It was determined that upon nitriding chromo-titanium alloys films will be formed, containing the double nitride Cr – Ti – N [337]. The kinetics of the nitridation process of titanium alloys with 5% Cr were investigated in [925].

Titanium - molybdenum - nitrogen [439, 226]. Alloys of the TiN – Mo system are produced by sintering mixtures of component powders by hot pressing at a temperature of 1750-1800°C. The alloys consist of two phases - molybdenum and titanium nitride, where their mutual solubility is not noticed. The alloys, containing 10-30% Mo (the remainder is TiN), have a density of 5.59-6.59 g/cm^3, $\sigma_{изг} = 28$-38 kg/mm^2. Hardness of alloys with 5-30 vol. % Mo is 1400-1500 kg/mm^2, at 400°C it descends to 764-913, at 800°C - to 540-608 kg/mm^2. The most scale-resistant are the alloys (cermets) with the least molybdenum content, in this case with 5% Mo.

Titanium - cobalt (nickel) - nitrogen, molybdenum - cobalt (nickel) - nitrogen. In these systems the ternary nitrides:

$Ti_{0.7}Co_{0.3}N$; $Ti_{0.7}Ni_{0.3}N$; $Mo_{0.8}Co_{0.2}N_{0.2}$ and $Mo_{0.8}Ni_{0.2}N_{0.9}$ have been detected. All of them have a WC type structure [916].

Transition metal – Al, Ga, In, Tl, Ge – nitrogen [419]. In these systems four groups of ternary compounds have been detected: Me_2XN, $Me_5Ce_3N_x$, Me_3X_2N, Me_2XN_x. The compounds of the first of these groups have a structure of the Cr_2AlC: Zr_2TlN, Hf_2InN, V_2GaN, V_2GeN type. Included in the second group are the compounds: $V_5Ge_3N_x$, $Nb_5Ga_3N_x$, $Ta_5Ga_3N_x$, $Ta_5Ge_3N_x$, $Ta_5Al_3N_x$ (stabilized by silicon), which, with the exception of the latter, have a structure of tye Mn_5Si_3 type; only $Ta_5Al_3N_x$ has a structure of the Cr_5B_3 type with vacancies at the sites of the nitrogen atoms. The connections V_3Zn_2N, V_3Ga_2N and Nb_3Al_2N have β-Mn type lattice, as the compounds Ti_2ZrN_x, Zr_2ZnN_x, Hf_2ZnN_x belong to the Ti_2Ni type.

The authors [420] produced the compounds Ti_2GaN, Ti_2InN, Zr_2InN by heating of mixtures of titanium or zirconium mononitrides with gallium or indium in a quartz ampule at 850°C for 500-850 h. They all have a Cr_2AlC structure with the following lattice constants and densities:

Phase	a, Å	c, Å	c/a	X-ray density g/cm^3
Ti_2GaN	3.00_4	13.30	4.42_8	5.73
Ti_2InN	3.07_4	13.97_5	4.54_7	6.52
Zr_2InN	3.27_7	14.84	4.52_6	7.49

One more group compose connection with a perovskite structure and the general formula Me_3XN [421]:

Phase	a, Å	X-ray density g/cm^3
Ti_3InN	4.190	6.15
Ti_3TlN	4.191	8.16

In works [422, 423] a detailed survey of the structure of phases

of the following types Me_3X_2N, $Me_5X_3N_{1-x}$, Me_2XN, Me_3XN_{1-x}.

Niobium-(hafnium, molybdenum, tungsten)-nitrogen. In work [1049] the solubility of nitrogen in niobium-rich alloys Nb-Hf, Nb-Mo, and Nb-W was investigated as a function of pressure and temperature. It was determined that hafnium, molybdenum and tungsten reduce the solubility of nitrogen in niobium. Thus, if at 2000°C and a nitrogen pressure of $2.8 \cdot 10^{-1}$ mm Hg the solubility of nitrogen in niobium is 9.4 at. %, then in a niobium alloy with 10% Hf or Mo it decreases to 1.0 at. %, and in a niobium alloy with 10 at. % W – to 6.8 at. % N.

Niobium-iron-nitrogen [431]. By investigating the solubility of NbN in γ-Fe in the temperature range of 1191-1336°C (with respect to the nitrogen content in the Fe-Nb alloys with 0-0.92 wt. % Nb, being in equilibrium with a gaseous mixture of nitrogen with 1% H_2) it was ascertained that the temperature dependence of the solubility product of NbH in γ-Fe is described by the formula

$$(\%\text{Nb})(\%\text{N}) = -10{,}230/T + 4{,}04.$$

The molar heat of solution of niobium nitride in γ-Fe is equal to 46.8 kcal.

Upon introducing a small quantity of iron into the niobium nitride both its electrical resistance, and also its TCR [temperature coefficient of resistance] increase. With an increase in the iron content the TCR decreases; for an alloy of NbH with 1% Fe the TCR in a broad range of temperatures is practically equal to zero (Fig. 134). Simultaneously a certain reduction in the coefficient of the thermo-emf of the niobium nitride occurs.

Tantalum-chromium (manganese, iron, cobalt, nickel)-nitrogen [428]. Alloys of these systems are prepared by nitriding mixtures of metal powders with dry ammonia at a temperature of 650-950°C for from two days to two weeks. The results of X-ray diffraction analysis are presented in Table 104.

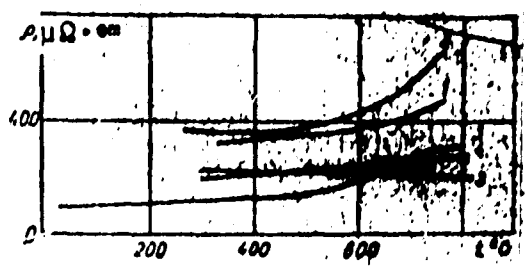

Fig. 134. The temperature dependence of the electrical resistance of the nitride NbN and the nitride with admixture of: 1 - NbN; 2 - NbN + 0.1% Fe; 3 - NbN + 0.05% Ti + 0.1% Fe; 4 - NbN + 0.5% Fe; 5 - NbN + 1% Fe.

Table 104. Phases, observed in binary alloys of tantalum nitride with Cr, Mn, Fe, Co, Ni nitrides.

System	Original alloy	Phases, formed by nitriding
Ta—Cr—N	$Ta_{0,75}$ $Cr_{0,25}$	X+TaN
	$Ta_{0,50}$ $Cr_{0,50}$	X + traces of unknown phase
	$Ta_{0,25}$ $Cr_{0,75}$	Cr(Ta)N+ traces of X-phase
Ta—Mn—N	$Ta_{0,90}$ $Mn_{0,10}$	$Ta(Mn)N_{0,8}$ + Ta-traces
	$Ta_{07,5}$ $Mn_{0,25}$	Ta_3MnN_4
	$Ta_{0,50}$ $Mn_{0,50}$	X + Ta_3MnN_4
	$Ta_{0,25}$ $Mn_{0,75}$	X + Mn-nitrides
Ta—Fe—N	$Ta_{0,80}$ $Fe_{0,20}$	Ta_3FeN_3+Ta
	$Ta_{0,67}$ $Fe_{0,33}$	Ta_3FeN_3
	$Ta_{0,50}$ $Fe_{0,50}$	Ta_3FeN_3 + Fe-nitrides
Ta—Co	$Ta_{0,80}$ $Co_{0,20}$	Ta_3CoN_3 + TaN
	$Ta_{0,67}$ $Co_{0,33}$	Ta_3CoN_3
	$Ta_{0,50}$ $Co_{0,50}$	Ta_3CoN_3 + α-Co
Ta—Ni—N	$Ta_{0,80}$ $Ni_{0,20}$	Ta_3NiN_3 + TaN
	$Ta_{0,67}$ $Ni_{0,33}$	Ta_3NiN_3
	$Ta_{0,50}$ $Ni_{0,50}$	Ta_3NiN_3 + Ni

In the Ta-Cr-N system a ternary phase (an X-phase was detected); its X-ray photograph has a complex character.

Tantalum nitride is soluble in chromium nitride, and the lattice constant of CrN varies from a = 4.149 kX ($CrN_{1.00}$) to a = 4.239 kX. The latter value corresponds to the maximum solubility of TaN in CrN (about 25 molar % Ta).

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In the Ta-Mn-N system two ternary phases are found, one of which is isostructural to the X-phase of the Ta-Cr-N system, and the other has a composition, expressed by the formula Ta_3MnN_4. Tantalum does not dissolve in $MnN_{0.61-0.63}$ (the η-phase), and manganese in ε-TaN.

Chromium-manganese-nitrogen. In the Cr-Mn-N system [438] a ternary compound of the composition $CrMn_3N_{3/4}\square_{1/4}$ (where □ is a vacancy). The formation of this phase causes an increase of two orders of magnetic susceptibility of alloys of chromium with manganese upon their nitridation. Hume-Rothery [441] indicates the existence of the ternary nitride $Cr_{56.1}Mn_{18.3}N_{25.6}$.

Molybdenum-cobalt-nitrogen [958-956]. The mixing of Mo_2N with 20% Co with subsequent pressing and sintering for 30 min in an ammonia medium at a temperature of 1500°C leads to the formation of an alloy, having a metallic character of fracture with a hardness of 86.5 R_c. A somewhat lower hardness is possessed by an alloy of 20% MoN, with a remainder made up of Mo_2C.

Molybdenum-zirconium-nitrogen [982]. In the Mo-Zr-N system alloys with 10, 30, 50, 70 and 90 at. % molybdenum were prepared, which were transformed into nitrides by nitridation with ammonia at 740°C. From pure zirconium up to a ratio of $Zr_{0.5}Mo_{0.5}$ a mixed nitride phase (Zr, Mo)N, will be formed, having a cubic face-centered structure, analogous to the structure of the nitride ZrN. The alloy $Zr_{0.1}Mo_{0.9}$ and molybdenum will form upon the nitridation a cubic face-centered phase – γ-$(Mo, Zr)_2N$. Close to the ratio of metals $Zr_{0.3}Mo_{0.7}$ both nitride phases will be formed, not mixing with each other.

Manganese-copper (zinc)-nitrogen [393]. The formation of solid solutions have been established to which it is possible conditionally to ascribe the compositions $Mn_{4-x}Cu_xN_{1-x/4}\square_{x/4}Mn_{4-x}Cu_xN_{1-x/4}\square_{x/4}$ (where □ are vacancies). An investigation of their structure and magnetic properties has been conducted.

Manganese-copper (silver, gallium)-nitrogen, chromium-gallium-nitrogen [429]. In the indicated systems ternary nitrides will be formed with the structure of perovskite, of which Mn_3CuN, Mn_3AgN and Mn_3GaN are products of the substitution of one manganese atom in the nitride Mn_4N by an atom of another metal, and Cr_3GaN is derivative of the hypothetical chromium nitride Cr_4N. The lattice constants of these phases are: Mn_3CuN a = 3.906; Mn_3AgN a = 4.019_5; Mn_3GaN a = 3.898; Cr_3GaN a = 3.875_5 Å.

Manganese-gallium (germanium, indium, tin)-nitrogen; iron-gallium (indium, tin)-nitrogen; cobalt-gallium (germanium, indium, tin)-nitrogen; nickel-gallium (germanium, indium, tin)-nitrogen [437]. From these systems ternary phases will be formed in the systems

$Co-Ga-N(Co_4Ga_3N)$, $Co-Ge-N(Co_{59,1}Ge_{20,5}N_{20,4})$;
$Co-In-N(Co_{61,5}In_{20,2}N_{18,3})$; $Co-Sn-N$; $(Co_{63}Sn_{21}N_{16})$;
$Ni-In-N(Ni_{65,7}In_{21,9}N_{12,4})$.

All these phases have a cubic structure of $L'I_2$ type with the constants indicated in Table 105. A ternary nitride will also be formed in the Fe-Ge-N system a tetragonal lattice (see Table 105). It has also been shown that Ga, Ge, In and Sn substantially expand the region of homogeneity of binary iron nitride (γ'-phase of the Fe-N system).

Table 105. Lattice constants of ternary nitride phases, A [437].

Phase	Crystal lattice	a	c	c/a
Co_4Ga_3N	Cubic	3,56—3,68	—	—
$Co_{59,1}Ge_{20,5}N_{20,4}$	"	3,57—3,61	—	—
$Co_{61,5}In_{20,2}N_{18,3}$	"	3,85—3,86	—	—
$Co_{63}Sn_{21}N_{16}$	"	3,82	—	—
$Ni_{65,7}In_{21,9}N_{12,4}$	"	3,84	—	—
$Fe_xGe_yN_z$	Tetragonal	5,318	7,733	1,454

A ternary compound has been detected in the Mn-Ga-N system [937]. It has the composition Mn_3GaN and is identical to the corresponding phases in the Cr-Ga-N, Mn-Cu-N and Mn-Ag-N systems (pages 411-412). This compound undergoes an antiferromagnetic transformation of the first order at 298°K.

Manganese-gold (mercury, tin, platinum, palladium, rhodium)-nitrogen. The existence of ternary compounds of the composition Mn_3Xn has been established with the structure of perovskite and following lattice constants [1033]:

Compound	a, Å	Compound	a, Å
Mn_3AuN	4.023_5	Mn_3PtN	3.968_5
Mn_3HgN	4.072_0	Mn_3PdN	3.979_6
Mn_3SnN	4.058_5	Mn_3RhN	3.928_0

The magnetic susceptibility and the magnetic transformation of these chemical compounds have been investigated.

Iron-chromium-nitrogen [930]. The composition of the nitrides and the heat of solution of nitrogen in alloys of iron with chromium have been determined. It has been demonstrated that chromium increases the solubility of nitrogen in α- and γ-Fe. At 600°C CrN will be formed with a lattice constant of a = 4.140 Å. Nitrogen stabilizes the γ-phase region in iron-chromium alloys.

Iron-chromium-nickel-nitrogen. The solubility of nitrogen in liquid Fe-Cr-Ni alloys has been investigated at a temperature of 1600°C and at a nitrogen pressure of 1 at (Fig. 135); the heats of solution have been determined [939].

Neodymium-aluminum (gallium, indium, thallium, tin, lead)-nitrogen [1063]. In these systems ternary nitride phases of the composition Nd_3MeN will be formed (where Me is Al, Ga, In, Tl, Sn, Pb) with a perovskite structure and lattice constants respectively of: 4.910; 5.06_3; 4.94_9; 4.95_7; 5.05_7; 5.06_7 Å.

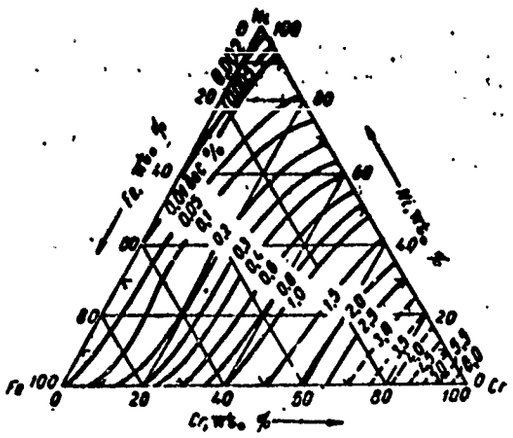

Fig. 135. The solubility of nitrogen in Fe-Cr-Ni alloys at 1600°C and at p_{N_2} = 1 at.

Uranium-plutonium-nitrogen [1028, 1041]. In the U-Pu-N system a continuous series of solid solutions will be formed, which are produced by sintering mixtures uranium and plutonium mononitrides. The nitriding of plutonium-uranium alloy proceeds with great difficulty; it is impossible to produce these solid solutions by fusion due to dissociation and the elimination of part of the nitrogen and metals.

2. Metal-Boron-Nitrogen Systems

Lithium (calcium, barium)-boron-nitrogen [913]. Upon heating mixtures of lithium nitride, calcium nitride or barium amide with boron nitride at a temperature of 700-1000°C the ternary nitrides Li_3BN_2, $Ca_3B_2N_4$ and $Ba_3B_2N_4$ will be formed. Their structure has not been investigated; a study of infrared-spectra indicates the presence in them of ion $N = B = N^{3-}$. Lithium boron-nitride melts at 870°C; its density is 1.755 g/cm^3; it has a black-violet color and it is very hard. Calcium boron-nitride is a white-colored substance with a yellowish tinge; it dissolves completely in dilute HCl; it is hydrolyzed in water with the liberation of ammonia (it is considerably more stable than lithium boron-nitride).

Titanium (zirconium, hafnium, niobium, chromium, tungsten, iron)-boron-nitrogen. In work [901] with the joint boriding and nitriding of niobium no ternary phases were detected.

The Ti-B-N system was investigated by G. V. Samsonov and Ye. V. Petrash [468] according to the section TiB_2-TiN within the limits of from 3 to 97 molar % of each component. The alloy samples were produced by hot pressing with subsequent annealing. The measurement of the melting points, carried out visually, made it possible to plot the fusibility curve for this system. A microscopic examination of the alloys showed that all the alloys before additional sintering and annealing are bi-phase. After annealing the two-phase alloys, containing 3-8 molar % TiB_2, becomes single-phase which can be connected with the solubility of titanium boride in titanium nitride.

The microhardness of the white (based on TiB_2) and yellow (based on TiN) phases practically does not depend on the composition of the alloys and is close to the hardness respectively of TiB_2 and TiN (Fig. 136). The same results are also given an X-ray investigation, the low accuracy of which could not make it possible to ascertain the solubility of the components. The latter is revealed by the electrical resistance-composition curve (Fig. 137). The thermal expansion in the TiB_2-TiN system is presented in Fig. 138.

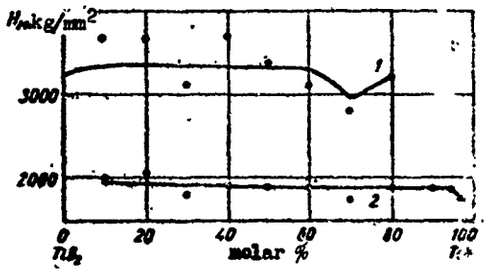

Fig. 136. Microhardness of alloys of the TiB_2-TiN system: 1 - phase based on TiB_2; 2 - phase based on TiN.

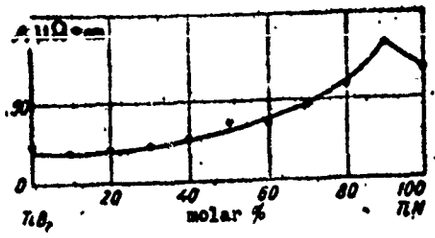

Fig. 137.

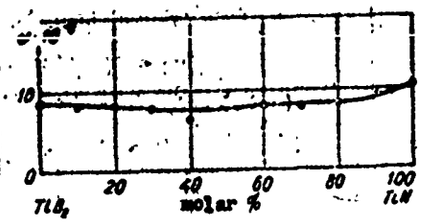

Fig. 138.

Fig. 137. Electrical resistance of the alloys of the TiB_2-TiN system.

Fig. 138. Coefficient of thermal expansion of the alloys of the TiB_2-TiN system.

Most resistant to oxidation is the alloy, containing 40-50% TiN (Fig. 139). Probably, the stablest film of titanium borate, protecting the samples is due to this composition. In alloys, containing large quantities of boride, being formed by oxidation the boric anhydride causes bubbling of the film. In alloys rich in TiN, the borate film is not continuous due to the intense liberation of nitrogen oxides by the oxidation of TiN by atmospheric oxygen.

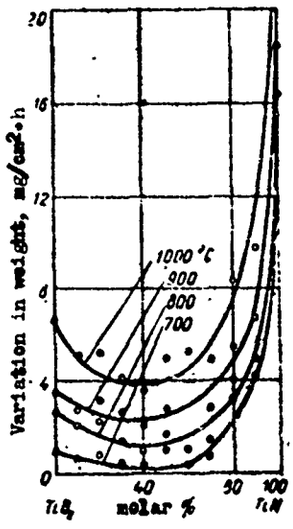

Fig. 139. The resistance to oxidation of the alloys of the TiB_2-TiN system.

Indications of the solubility of hexagonal TiB_2 in cubic TiN and the practical absence of the reverse solubility of TiN in TiB_2 were discovered which is reminiscent of the same phenomenon in the investigation of the solubility of WC in the cubic carbides TiC,

ZrC, NbC, TaC and VC. The difference in the chemical stability of TiB_2 and TiN is less than between WC and TiC, therefore the region of solubility of TiB_2 and TiN is considerably less than WC in TiC.

The investigation of the Ti-B-N system was continued in work [903], where it was confirmed that there are no ternary compounds in the system.

In the investigated Zr-B-N system in an analogous manner [904] ternary compounds were also not detected, but the formation of Zr-N-B solid solutions of the composition $Zr(N, B)_{1-x}$ was shown, where about 37 at. % of the N can be replaced by boron. An analogous phase of solid solutions also exists in the Hf-B-N system [904], where the boundaries of single-phosicity intensely depend on temperature.

In work [416] the following regions and section of the Zr-B-N system were investigated: $Zr-ZrB_2-ZrN$, ZrB_2-B-BN, $ZrN-ZrB_2-BN$, ZrB_2-ZrN, ZrB_2-BN. To prepare the samples mixtures of zirconium hydride, zirconium nitride, boron nitride and boron were subjected to hot pressing with subsequent homogeneous annealing for 4-6 h at a temperature of 1400-1900°C (depending upon the composition) in an argon medium. As a result metallographic and X-ray diffraction investigations it was established that ternary phases are not formed in this system. In zirconium diboride, having an insignificantly small region of homogeneity, neither carbon nor nitrogen are dissolved. With small contents of zirconium in the system two-phase regions of ZrB_2-BN and a solid solution (ZrN-ZrB)-BN will be found at temperatures lower than 1600°C. With contents in the medium region, i.e., ∿50 at. % Zr, 25 at. % B and ∿25 at. % N, three phases are detected: the α-solid solution based on zirconium, ZrB_2 and the solid solution (ZrN-ZrB). In melted samples in the ZrB_2-BN-B region the phase ZrB_{12} is detected. In section ZrN-BN, ZrB_2 is mainly observed, which is formed according to the reaction:

$$ZrN + 2BN = ZrB_2 + 3/2N_2.$$

which agrees with the previous observations of Brewer and Haraldsen [417]. An investigation of the solid solutions of ZrN-ZrB shows that the dissolution of ZrB in ZrN mainly occurs.

Kiessling and Liu [320], in treating various borides of chromium, iron tungsten with ammonia at high temperatures, discovered that with this the decomposition of the borides occurs and nitrides of metals and boron will be formed. The stability of the original borides strongly depends on their composition and for the iron and chromium borides it increases with the increase in the boron content in the phase.

In the Cr-B-N system all the chromium borides, discovered by Kiessling in his time were subjected to nitridation with ammonia: $\delta(\sim Cr_2B)$, $\varepsilon(Cr_3B_2)$, $\xi(CrB)$, $\eta(Cr_3B_4)$ and $\Theta(CrB_2)$.

The phases, produced by nitriding for 10 h, are given in Table 106 (the phases, containing chromium, are enumerated in the order of descending chromium concentration; boron nitride is shown last).

Table 106. Results of the nitridation of chromium borides [320].

Temperature, °C	$\delta(\sim Cr_2B)$	$\varepsilon(Cr_3B_2)$	$\xi(CrB)$	$\eta(Cr_3B_4)$	$\theta(CrB_2)$
552	Cr_2B	Cr_3B_2	CrB	Cr_3B_4	CrB_2
735	$Cr_2B+CrN+BN$	Cr_3B_2	CrB	Cr_3B_4	—
800	$Cr_2B+CrN+BN$	Cr_3B_2+CrN	CrB	Cr_3B_4	CrB_2
900	—	$CrN+Cr_2N+BN$	CrB+CrN	Cr_3B_4	—
954	$CrN+Cr_2N+BN$	—	—	—	CrB_2
1000	—	$CrN+Cr_2N+BN$	CrB+CrN+BN	—	CrB_2
1050	$CrN+Cr_2N+BN$	—	CrN+CrN+BN	$Cr_2N+Cr_3B_4$	—
1100	—	—	—	Cr_2N+BN	CrB_2+CrN
1180	Cr_2N+BN	Cr_2N+BN	Cr_2N+BN	Cr_2N+BN	Cr_2N+BN

Thus, in the order of increasing resistance to the effect of nitrogen the phases of the Cr-B system can be arranged in the following series: Cr_2B (735°C), Cr_3B_2 (800°C), CrB (1000°C), Cr_3B_4 (900-1000°C) and CrB_2 ($\sim$1100°C). The resistance to nitrogen increases with the composition of the elements of the structure of boron atoms.

Concerning the Fe-B-N system sufficiently exact data have not been obtained, but greater resistance to the effect of nitrogen, apparently, is possessed by iron boride FeB (Table 107), in the structure, which are boron chains, whereas in the structure of Fe_2B of the boron atoms are isolated from each other.

Table 107. Results of the nitridation of iron borides [320].

Temperature °C	Fe_2B	FeB
352	Fe_2B	FeB
400	ξ-фаза+BN	Fe_2B+ξ+BN(?)
448	ε+BN	—
505	ε+γ'+BN	—
550	γ'+ε+BN	γ'+ε+BN
602	α-Fe+γ'+ +ε+BN	γ'+ε+α+ +Fe+BN
702	α-Fe+BN	—
768	α-Fe+BN	α-Fe+BN

In work [902] the solubility of nitrogen in iron-boron melts was investigated. The formation here of boron nitride was detected.

In the W-B-N system all three bodies – W_2B, WB and W_2B_5 (Table 108) were subjected to nitridation. A noticeable increase in the stability of the borides with a increase in the number of B-B bonds was not detected in this system: all the borides begin to interact with nitrogen at a temperature of 800-900°C with the formation of the nitrides W_2N (the β-phase of Kiessling), BN, and also of the cubic nitride γ-phase of the W-N system, discovered in the same work by Kiessling (concerning the W-B-N system see also [1109, 1110]).

Table 108. The results of the nitridation of tungsten borides [320].

Temperature °C	W_2B	WB	WB_2
700	W_2B	WB	WB_2
750	W_2B	WB	WB_2
800	W_2B	WB+BN	—
850	W_2B+α-W+(γ+BN)	α-W+BN+(γ+BN)	α-W—(WB_2)+(γ+BN)
900	α-W+(W_2B)+BN	α-W+(WB)+BN	α-W+(WB_2)+BN
1000	α-W+(W_2B)+BN	α-W+BN	—
1100	α-W+BN	α-W+BN	α-W+BN

3. Metal-Carbon-Nitrogen Systems

Calcium-carbon-nitrogen. An investigation of the interaction between calcium carbide CaC_2 with nitrogen [240] at temperatures of 850-1100°C and in the presence of various accelerating admixtures ($CaCl_2$, CaF_2, BaF_2 and others) showed that the interaction reaction is linear and is of the first order with respect to pressure. This makes it possible to draw a conclusion about the fact that the nitridation of calcium carbide is a typical topochemical reaction. As a result mixtures of $CaCN_2$ + C are formed.

Aluminum-carbon-nitrogen. In this system the existence of the ternary carbonitrides $Al_6C_3N_2$, $Al_7C_3N_3$, $Al_8C_3N_4$ has been reliably established, and also the existence of the compounds $Al_9C_3N_5$ and $Al_{10}C_3N_6$ is assumed [908], i.e., the presence of a homologous series of connections with the general formula $(AlN)_n \cdot Al_4C_3$. The character of the basic properties of these compounds in comparison with the properties of aluminum nitride and carbide are given, according to [908, 909], in Table 109.

Table 109. The structure and density of aluminum carbonitrides.

Compound	Number of atoms in the unit cell	Space group	Lattice constant			Density g/cm³	
			a	c	c/a	calculated	pycnometric
AlN	2	$P6_3mc$	3,111	4,978	1,600	3,262	3,20
Al_4C_3	3	$R\bar{3}m$	3,330	24,89	7,474	3,000	2,93
Al_3C_3N	2	$P6_3mc$	3,281	21,67	6,005	3,039	2,99
$Al_6C_3N_2$	3	$R\bar{3}m$	3,248	40,03	12,33	3,076	3,04
$Al_7C_3N_3$	2	$P6_3mc$	3,226	31,70	9,826	3,102	3,046
$Al_8C_3N_4$	3	$R\bar{3}m$	3,211	55,08	17,15	3,133	3,05
$Al_9C_3N_5$*	2	$P6_3mc$	3,197	41,69	13,04	3,141	3,06
$Al_{10}C_3N_6$*	3	$R\bar{3}m$	3,186	70,00	21,97	3,157	3,07

*Assumed compounds.

Transition-metal carbonitride systems. A large part of the transition-metal carbides and nitrides of groups IV and V form a continuous series of solid solutions, with the exception of alloys with TaN, having a hexagonal structure and certain alloys with VN and VC with lattice constants of other carbides and nitrides.

The data on the mutual solubility of the nitrides and carbides of groups IV and V are brought together, with respect to Kieffer [333], in Table 110.

Table 110. The mutual solubility of transition-metal of groups IV and V.*

Connections	TiC	ZrC	HfC	VC	NbC	TaC
TiN	A	(A)	(A)	A	A	(A)
ZrN	A	A	(A)	Б	Б	(A)
HfN	(A)	(A)	(A)	(A)	(A)	(A)
VN	A	(B)	(A)	A	A	(A)
NbN	A	(A)	(A)	A	A	(A)
TaN	(B)	(B)	(B)	(A)	(B)	B

*A - complete mutual solubility; Б - the absence of or very little solubility; B - the solid solution region on the part of the cubic phase. The probable characteristics of the unexamined systems are given in parentheses.

The results of the experimental investigation of mixed carbonitride systems are given according to [177, 244], in Figs. 140-142. Moreover in the TiN-VC, TiN-NbC, ZrN-TiC, VN-VC, VN-NbC, VN-TiC, NbN-TiC, NbN-VC, NbN-NbC systems continuous solubility has been established, and in the ZrN-VC and ZrN-NbC systems - limited and low solubility.

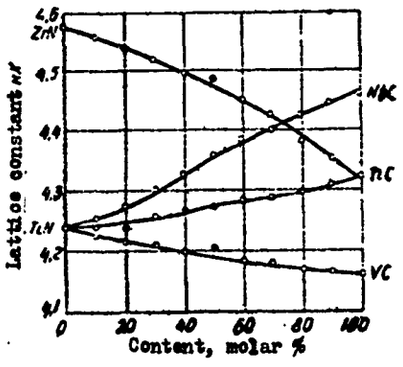

Fig. 140.

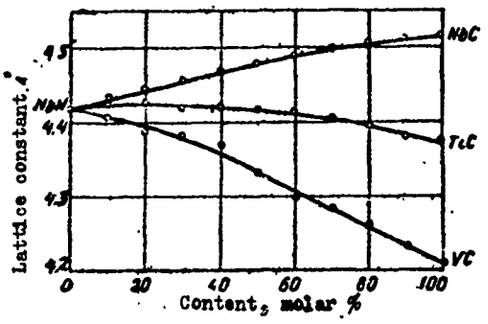

Fig. 141.

Fig. 140. Variation in the lattice constant in TiN (ZrN)-TiN (VC, NbC).

Fig. 141. Variation in lattice constant in the NbN-TiC (VC, NbC).

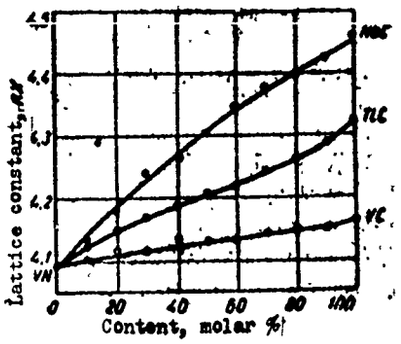

Fig. 142. Variation in the lattice constant in VN-TiC (VC, NbC) systems.

The most detailed data on the number of systems of this type are given in work [978], where the preparation conditions, the structure and the physical properties of the TiC-ZrN, TiC-TaN, ZrC-NbN, ZrC-TaN, ZrN-NbC, NbN-TaC systems were investigated. They are all systems with a continuous series of solid solutions, with the exception of the TiC-TaN and ZrC-TaN systems, in which the solid solutions in the region up to a TaN content respectively of 80 and 85 molar %. In the TiC-TaN, TiC-ZrN, ZrC-NbN systems the variation in the molar magnetic susceptibility is monotypic - it smoothly increases from the negative values for the corresponding carbides to the positive values for the nitrides; this variation in all cases is nonlinear with the intersection by the susceptibility curve of the axis of compositions at ∿20 molar % of nitride component.

An investigation of systems of mononitrides with monocarbides was carried out in [905]. The formation of a continuous series of solid solutions in the TiC-ZrN, TiC-NbN, ZrC-ZrN, ZrC-NbN, ZrN-NbC, NbC-NbN, NbN-TaC systems was confirmed. Hexagonal TaN dissolves in TiC up to 70 molar % and in ZrC up to 80 molar %. An investigation of the magnetic susceptibility of these alloys showed that the effect of carbon in the nitride in general is considerably less expressed than nitrogen in the carbide.

An analogous investigation of a number of monocarbide and mononitride systems is given with the participation of hafnium and it is demonstrated that in systems of HfN with TiN, ZrN, TiC, ZrC, HfC, NbC, TaC and also in systems of HfC with TiN, ZrN, NbN a continuous series of solid solutions will be formed [906]. The

nitrides VN and TaN significantly dissolve in HfN, and the dissolution of TaN in HfC is also considerable.

In works [232, 255] the kinetics of the replacement of nitrogen is titanium, zirconium and hafnium were investigated by carbon nitrides.

Titanium-carbon-nitrogen. Carbide titanium TiC will form with titanium nitride TiN a continuous series of solid solutions [175]. The results of an X-ray diffraction investigation of TiN-TiC alloys, prepared by heating mixtures of TiN + TiC for 4 h at a temperature of 2425°C [177], makes it possible to consider that the lattice constant varies with composition practically according to the Vegard rule (see Fig. 140). The single-phasicity of an alloy, corresponding to the empirical formula $Ti_{10}N_8C_2$ and having a lattice of the NaCl type with a constant of 4.243 kX, was established earlier. Crystals of titanium carbonitrides, extracted from steel, containing, 0.1-1% C and up to 6% Ti, had compositions over a wide range of from almost pure TiN to almost pure TiC [243]. In the slags of blast furnaces upon the melting of high-titanium charges titanium carbonitrides are present [191]. Due to the high melting point they vigorously reduce the fluidity of the slags.

The properties of TiN-TiC alloys were investigated in detail in works [126, 170, 830]. In the transition from TiN to TiC the value of the coefficient of thermo-emf increases, passing into the region of TiC content of the order of 25 molar % through a small relative maximum. The behavior of the specific electrical resistance also reveals a rather sharp maximum of electrical resistance at 20-30% TiC. The Hall coefficient on the contrary, increases monotonically. The thermal coefficient of electrical resistance in the transition to 70-80 molar % TiC displays a maximum, and then decreases somewhat to pure TiC (Fig. 143). The magnetic susceptibility sharply decreases with the dissolution of TiC in TiN (see Fig. 16 [830]). An investigation of the temperature dependence of the Hall constant of titanium carbonitrides with a low nitrogen content ($TiC_{0.965}N_{0.009}$; $TiC_{0.961}N_{0.025}$; $TiC_{0.948}N_{0.047}$; $TiC_{0.930}N_{0.075}$; $TiC_{0.952}N_{0.042}$)

was carried out in work [798]. It was demonstrated that with an increase in temperature in the region of up to 300°K the deviation in the values of the Hall coefficient decreases to practically full disappearance of this difference at ∿300°K.

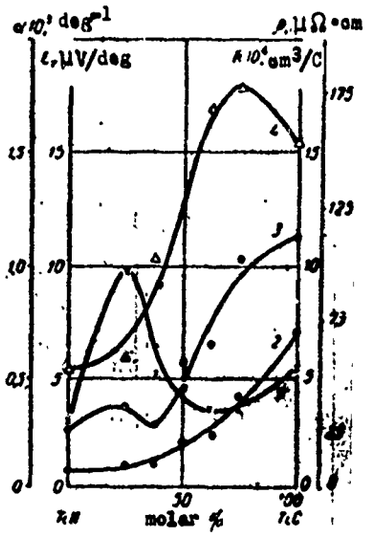

Fig. 143. Physical properties of alloys in the TiN-TiC system: 1 - specific electrical resistance; 2 - Hall coefficient; 3 - thermo-emf coefficient; 4 - thermal coefficient of electrical resistance.

The kinetics of the replacement of nitrogen by carbon in the Ti-N-C system were investigated in work [232].

Zirconium (hafnium)-carbon-nitrogen. Investigations of certain electrophysical properties of alloys of the ZrC-ZrN system [789] showed the metallic nature of their conductivity at least up to a temperature of 300°K (with a low thermal coefficient of electrical resistance), and also the weak temperature dependence of the Hall constant in this region. An analogous investigation was carried out in the same work for certain alloys of the HfC-HfN system.

According to [978], the molar magnetic susceptibility in the ZrC-ZrN system monotonically and nonlinearly increases from a negative value for ZrC ($-20.3 \cdot 10^{-6}$) to a positive value for ZrN ($+22 \cdot 10^{-6}$).

Vanadium-carbon-nitrogen. In the V-VC-VN system at a temperature

of 110-1400°C [433] three different phases were detected: the metallic α-phase, two carbonitrides - the hexagonal β-phase (type L'_3) $V_2(C, N)$ and the cubic δ-phase (type B_1) V(C, N). The two regions of existence of these phases are shown in Fig. 144 [1082].

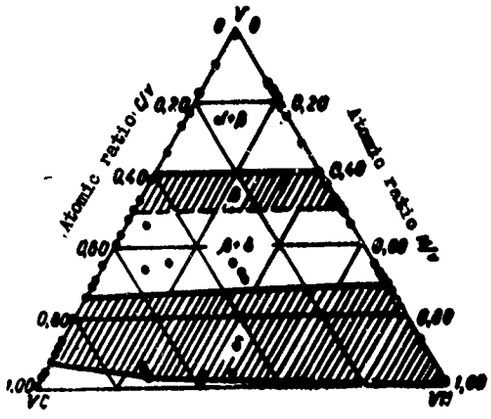

Fig. 144. Phases of the ternary system V-VC-VN in the temperature range 1100-1400°C: o are single-phase; ● are two-phase.

Niobium-carbon-nitrogen. In works [920, 923] the phase diagram of the Nb-NbC-NbN system was plotted, depicted in Fig. 145 (the isothermal section is at 1250-1450°C). As follows from these data, there are two regions of carbonitride phases in the system. The region of existence of the cubic δ-phase of the NaCl type has the shape of a broad band between the binary phases of the same type. The carbonitride β-phase, having hexagonal tightest packing of the metal, also spreads through the whole ternary region and connects both binary compounds of identical structure – Nb_2C and Nb_2B. The positions of the phase borders depicted in Fig. 145 correspond to nitridation, carried out at a temperature of 1250-1300°C and at a nitrogen pressure of 1 at. By nitriding at a nitrogen pressure of 4.5-5 at., a temperature of 1450°C and an exposure of 1.5-2 h, a mixture of niobium and niobium carbide or by homogenization under the indicated conditions of mixtures of niobium carbide and nitride in work [966] solid solutions of NbC-NbN (carbonitrides) were produced in a broad region of compositions, and it was also shown that maximum critical temperature of transition to superconductivity, equal to 17.9°K to the composition $NbC_{0.3}NbN_{0.7}$ corresponds. An

electron concentration of about 4.85 valence electrons per atom corresponds to the same composition. Presence of maximum T_k is connected with the presence of a maximum density of electron energy states at the Fermi surface at the indicated electron concentration.

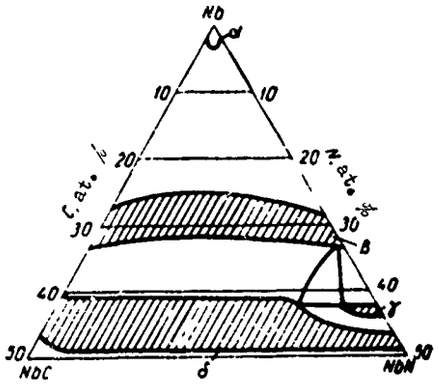

Fig. 145. Phases of the ternary system Nb-NbC-NbN at 1250-1450°C.

Concerning the superconductivity of cubic niobium carbonitride see also work [1018].

The molar magnetic susceptibility of alloys in the NbC-NbN system increases rather steeply from $18 \cdot 10^{-6}$ for NbC to $\sim 30 \cdot 10^{-6}$ at a NbN content of 40 at. %, after which with a subsequent increase in the niobium nitride content (up to 100 molar %) it practically does not vary [978].

Niobium carbidonitride (δ-phase) forms in a heat-resistant alloy based on cobalt, containing 1% Nb and 0.20% C.

Tantalum-carbon-nitrogen. The authors [526] detected the continuous series of solid solutions Ta_2C-Ta_2N. The solubility of TaN in $TaN_{0.80-0.90}$ (δ-phase) is of the order of 5 at. %, and the solubility of TaC in TaN is very small; solubility of TaN in TaC was not found. Ternary nitride phases also were not detected.

In work [923] the ternary system Ta-TaC-TaN was investigated. The following phases were found: the metallic α-phase with a cubic

body-centered structure (dissolving up to 5 at. % carbon and nitrogen), the β-phase with hexagonal dense packing (existing in two crystalline forms), the ξ-phase with an unknown structure and the hexagonal η-phase corresponding to $TaC_{0.64}$ or $TaN_{1.00}$, the δ-phase of the NaCl type, corresponding to the structure of TaC (Fig. 146).

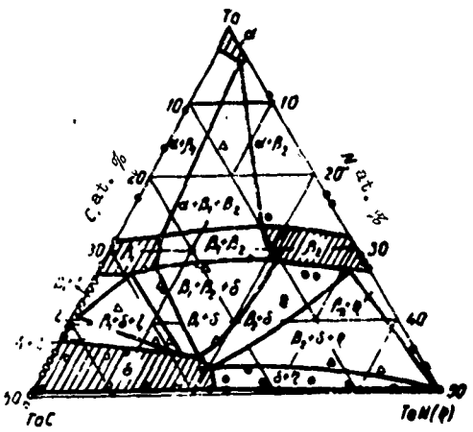

Fig. 146. Phases in the ternary system Ta-TaC-TaN at 1250-1450°C: o are single-phase; ● are two-phase; Δ are three-phase.

Chromium-carbon-nitrogen. In work [434] it was demonstrated that in the carbidizing of chrome coatings in a medium, containing nitrogen, on chromium a layer of chromium nitride Cr_2N will be formed, then follows a layer of chromium carbide Cr_7C_3 and, finally, an external carbide layer of Cr_3C_2. In connection with the presence of a hexagonal structure for the nitride Cr_2N and the carbide Cr_7C_3 they dissolve to a limited degree in each other. Researchers [435] sintered mixtures of the powders Cr_3C_2 and Cr_2N by the hot pressing method at 1500°C. By an X-ray diffraction investigation the existence of chromium carbonitride of the composition $Cr_2N_{0.3}C_{0.6}$ was detected which is a derivative of the chromium nitride Cr_2N (replacement of part of the nitrogen atoms by carbon atoms). Another chromium carbonitride is a derivative of the chromium carbide Cr_7C_3 and has a composition, described by the formula $Cr_7C_{2.7}N_{0.5}$. One more carbonitride $Cr_2N_{0.6}C_{0.3}$ is the ordered saturated solid solution of nitrogen and carbon in chromium and it is that solution, which is formed by treating chromium with nitrogen and carbon, detected in work [434] on the boundary of the Cr_2N and Cr_7C_3 layers.

A more detailed study of the Cr-C-N system was carried out by Ettmayer [1021], which investigated the two isothermal sections by the X-ray diffraction method at temperatures of 1100 and 1400°C, at pressures of from 1 to 30 at. As a result it was established that chromium carbides practically do not dissolve nitrogen, and chromium mononitride does not dissolve carbon; whereas the nitride dissolves considerable quantities of chromium carbide. At high nitrogen pressure the ternary compound of the approximate composition $Cr_{0.62}C_{0.35}N_{0.03}$ was detected, having a rhombic structure (a = 6.952; b = 9.255; c = 2.845 Å).

According to [993], in the chromium-carbon-nitrogen system the compound $Cr_3(C, N)_2$ exists (space group D_{2h}^{17}, the structure of which is related to the structure of Cr_3C_2 (it contains octahedral and trigonal-prismatic structural elements).

A newly conducted investigation of the phases forming in the Cr-C-N system [1056] showed the presence of carbonitrides phases of Cr_2CN (the hexagonal ε-Fe_2N type; a = 4.83 to 4.85; c = 4.48 to 445 Å; the density is 6.44 g/cm^3; there exists up to 15% C in the alloys); Cr_2CN (the rhombic ξ-Fe_2N type; a = 4.85; b = 5.60; c = = 4.44 Å; the density is 4.44 g/cm^3) and Cr_3CN_2 (a rhombic, structural type with the space group D_2^{17}; a = 6.95; b = 9.25; c = 2.84 Å; the density is 6.50 g/cm^3; it melts incongruently at 1600°C; the Vickers hardness is 1600 kg/cm^2).

Molybdenum-carbon-nitrogen [427]. Upon the interaction of molybdenum with CO and nitrogen at 450-850°C only mixtures of β- and δ-molybdenum nitride will be formed; the formation carbonitrides has not been established (cyanogen and dicyanogen are contained in the exhaust gases).

Tungsten-carbon-nitrogen. In work [838] reaction diffusion was investigated in the W-C-N_2 system. It was demonstrated that in this case only binary phases will be formed, where in the presence of nitrogen the process of the diffusion of nitrogen into tungsten is inhibited.

Manganese-carbon-nitrogen. Upon the interaction of the nitride with manganese carbide and metallic manganese at 1000°C (from 8 to 28 h) manganese carbonitride will be formed $Mn_4N_{1-x}C_x$ with x = = 0.102-0.798 and with an increase in this region of the compositions of the Curie point from 515 to 626°C will be formed [393].

Iron-carbon-nitrogen. This system was investigated by Bridelle and Michel [432]. Alloys prepared by nitriding the iron carbide Fe_3C with ammonia at a temperature of 400-500°C for 1-70 h, by carburizing iron nitride (γ-phase) at 450°C with a mixture of H_2 + CO, and also by simultaneously carburizing and nitriding Fe_2O_3 at 450-550°C.

In all cases the formation of the ternary compound $Fe_xN_xC_z$ was detected with a hexagonal lattice, the constants of which are: a = = 2.749; c = 4.400 kX. The exact composition of this phase remains undetermined; apparently, it has a rather broad region of homogeneity both with respect to the content of nitrogen, and also of carbon. Jack [924] indicates that this region of homogeneity stretches from Fe_8N_4 to Fe_8C_3N. The latter is isomorphic to Fe_2N. In the patent [430] methods of producing iron carbonitride by heating mixtures of pure iron powder with cyanide salts of alkali metals at 750°C are discussed.

The scheme of the basic reaction in the Fe-C-N system is given in work [936].

Uranium (thorium)-carbon-nitrogen. An X-ray diffraction investigation of mixtures of UC-UN and ThC-ThN powders, heated in an argon medium at 1600°C for 4 h was made [935]. In the ThC-ThN system a continuous series of solid solutions will be formed with practically an exact correspondence in the variation in the lattice constant to the Vegard rule. In the analogous UC-UN system two phases are observed, one of which is the solid solution UC-UN.

On the other hand, as was noted in [1041], with the correct selection of the conditions of homogenization uranium monocarbide and mononitride will form a continuous series of solid solutions without the appearance of any additional phases.

The authors [1055] present additional data on the U-C-N system and the properties of uranium carbonitrides as promising materials of dispersed nuclear fuel.

Uranium-plutonium-carbon-nitrogen [1041]. In the UC-PuN system a continuous series of solid solutions will be formed. Variations in the lattice parameters differ insignificantly from the Vegard rule.

4. Metal-Oxygen-Nitrogen Systems

Lithium-titanium (germanium, silicon)-oxygen-nitrogen [425]. Upon melting Li_3N with TiO_2 and TiN (or Li_2O) oxynitrides of the general formula will be formed: $Li_5TiN_3 \cdot xLi_2O$ (x = 0.5; 0.9; 1.6; 2.0; 5.2), having a structure of the fluorite type with the lithium and titanium atoms in the positions of fluorine, and nitrogen and oxygen atoms in the positions of calcium. Oxynitrides of $Li_5SiN_3 \cdot Li_2O$ and $Li_5GeN_3 \cdot 2Li_2O$ will be formed in an analogous manner. They are readily soluble in dilute acids; they are similar in properties to the ternary nitrides Li_5XN_3 (where X = Ti, Ge, Si).

Aluminum (gallium, germanium)-oxygen-nitrogen. Aluminum oxynitride $Al_{\frac{3+x}{3}}\square_{\frac{1-x}{3}}O_{4-x}N_x$ will be formed by substituting oxygen atoms and it contains a considerable fraction of □ defects [538]. This oxynitride is designated as the γ-phase of the Al-O-N system. Furthermore, one more oxynitride has been detected: the δ-phase analogous in structure to δ-Al_2O_3 with the lattice constants a = 7.943; c = 11.72 A. With a decrease in nitrogen content the lattice becomes rhombic with the constants a = 7.943; b = 7.962; c = 11.71 Å.

In the Ga-O-N system no oxynitride phases were detected, and in the Ge-O-N system the existence of an oxynitride of the composition $Ge_6O_9N_2$ was established with a large number of lattice defects. Its structure is analogous to the structure of rutile; the lattice constants are a = 4.395; c = 2.864 Å.

Calcium-oxygen-nitrogen. Samples of calcium carbonitride with the structure of CaO and a composition, varying from $CaO_{0.944}N_{0.024}$ (a = 4.8192 Å; the pycnometric density is 3.283; the X-ray density is 3.294 g/cm^3), $CaO_{0.932}N_{0.029}$ (a = 4.8216 Å, the pycnometric density is 3.287; the X-ray is 3.283 g/cm^3) were obtained in work [967] by heating CaO in Ca and N_2 vapors, which are formed as a result of the dissociation of Ca_3N_2 at 1100°C in a hermetic iron container. These products are examined as a solid solution of the nitride Ca_2N (or, possibly, Ca_5N_2) in CaO; it has a high electrical resistance. Similar phases were detected in Sr(Ba)-O-N and Ca-S-N systems.

Titanium-oxygen-nitrogen. Stone and Margolin [921] investigated the phase diagrams for samples, obtained by treating molten titanium iodide in an arc furnace with NO. The alloys were homogenized, annealed with subsequent quenching in water. At a temperature of 1770°C a ternary peritectic reaction is observed, the Ti-N-O system is characterized by regions of α-, β- and α + β-phases, which expand with an increase in temperature. It was determined that the addition of oxygen to Ti-N alloys reduces the effect of nitrogen as a stabilizer of the α-phase.

The dependence of the lattice constant on the composition in the TiO-TiN system was determined in work [77]; this dependence compared with the shape of the density curve of samples, annealed at 1700°C. In the region from 0 to 60 molar % TiN the lattice constant increases, and then, having attained a value of a_{TiN}, remains constant. The density during the variation in the composition from 0 to 30 molar % TiN drops; at 30-60 molar % TiN it increases linearly, and subsequently remains constant. These data

are explained by the fact that up to the composition of $TiO_{0.7}N_{0.3}$ the formation of a solid solution occurs, and up to $TiO_{0.4}N_{0.6}$ the defect sites are filled (in TiO, according to Ehrlich [135], about 16% of the defects). In the region above 60 molar % TiN a heterogeneous mixture of $TiO_{0.4}N_{0.6}$ and TiN will be formed.

A detailed investigation of the physical properties of the alloys of this system was carried out in work [174] (Table 111). On the curves of the concentration dependence of electrical resistance, the coefficient of thermo-emf, the Hall coefficient minima are detected, corresponding to approximately 20-30 molar % TiO in the alloys.

Table 111. The composition and the results of the measurements of the electrical properties of alloys of TiN-TiO.

Content molar %		Specific electrical resistance, μΩ·cm	Hall coefficient $R \cdot 10^4$, cm^3/C	Coefficient of thermo-emf, mV·deg
TiN	TiO			
100	0	26	—0,67	—9,3
90	10	17,9	—0,4	—7,1
79,6	20,4	13,1	—0,17	—6,4
73,1	26,9	11,3	—0,48	—6,75
65,0	35,0	12,1	—0,82	—
62,7	37,3	12,7	—1,36	—8,6
47,6	52,4	14,2	—1,64	—
46,7	53,3	—	—1,70	—13,4
46,0	54,0	14,3	—2,02	—
41,8	58,2	27,0	—2,64	—

As follows from the data on the variation in the electrical resistance for the section of the TiN-TiO system, the addition of TiO to TiN at first causes a rather sharp decrease in the electrical up to a TiO content of 25-30 molar %, after which the resistance again slowly increases to 50-55 molar % TiO, when this increase becomes acute. Such behavior in the variation of the property is usually characteristic for cases of the mutual effect of two competing factors, which in this case, obviously are the atomic

radius and the ionization potential of oxygen. With small admixtures of oxygen its smaller ionization potential (13.57 eV) plays the basic role as compared to the nitrogen atom (14.51 eV), which facilitates the transfer of electrons due to the oxygen atoms into the conduction band and decreases the total negative polarization of the energy complexes of the lattice, consisting of nitrogen and oxygen atoms. However the effect of the geometry factor - the larger simultaneously increases, which causes a gradual decrease in the overlapping of the energy bands, accompanying the increase in the lattice constant of the solid solution. Beginning with 30 molar % TiO this factor acts to an even greater degree which causes a gradual increase in resistance, and in the region of 50 molar % TiO a sharp increase in resistance occurs due to the predominance of oxygen atoms in the lattice of the solid solution and the unique "inversion of phases," when titanium oxide becomes the solvent and not the dissolved component. An important role is also played, arrarently, by the ability of the oxygen atom to transfer to the bond only two electrons as compared to the three electrons for the nitrogen atom.

A minimum of emf for a TiO content of 20 molar % and its coincidence with the minimum on the electrical resistance-composition curve agrees well with the concepts, consisting of the fact that thermo-emf decreases with respect to absolute value with an increase in the degree of overlapping (erosion) of the energy bands.

With respect to a concentration variation in the Hall coefficient of up to 20 molar % TiO, it is possible to assume a relative increase in the hole fraction in the process of electrical conductivity which agrees with the decrease in the absolute value of the negative value of the thermo-emf. Conversely, beyond 20 molar % TiO the hole contribution to electrical conductivity decreases. From Fig. 147 it follows that all the investigated alloys upon achieving a definite temperature change the sign of the temperature coefficient of electrical resistance to the negative, where this temperature in general increases with the increase in the nitrogen content in the solid solution with a simultaneous decrease in the

absolute value of the maximum electrical resistance. Previously the temperature transition through the maximum of alloys rich in TiO, was connected, obviously, with the role of the geometric factor - the larger dimension of the ionic radius of oxygen, leading to a reduction in the erosion of the energy bands. The diverse nature of the maxima on the curves is noted - probably, the sharp maxima correspond to the predominant affect of one of the nonmetals (oxygen or nitrogen), and the relatively flat ones - to their mutual affect, close with respect to the final result to each other.

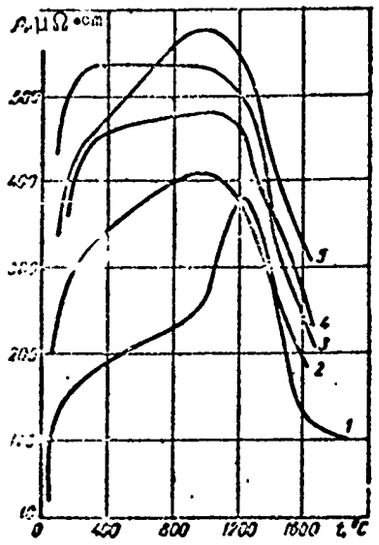

Fig. 147. The temperature-concentration dependence of the electrical resistance.

In work [1066] the enthalpy of the formation titanium oxynitrides TiN_xO_y with the sum of indices for nitrogen and oxygen, equal to 1; 0.8; 0.7, was determined. It was demonstrated that the enthalpy of the formation of the oxynitrides is composed by adding the enthalpies of the formation of TiN and TiO.

Zirconium-oxygen-nitrogen. In this system oxynitrides of the general composition $ZrO_{2-2x}N_{x+y}$ were detected [440, 538].

The results of an investigation of a reaction between ZrO_2 and ammonia [440] showed that at 950°C the formation of a white-colored phase (according to the designations of [440] - the β-phase) is

observed; with a more protracted reaction - the formation of the yellow-colored γ-phase but with the heating of zirconium dioxide in a stream of ammonia at higher temperatures, for example at 1100°C, the γ-phase decomposes with the formation of the β-phase and the nitride ZrN. Finally, at very high temperatures (above 2000°C) the β-phase decomposes and the nitride ZrN forms, and also the β'-phase, the structure of which is reminiscent of the structure of the β-phase. The phases β, β', γ are stable at the temperatures of their formation only in a nitrogen medium, and when heated in an inert medium (for example, argon) they decomposes with the formation of zirconium nitride and monoclinic ZrO_2. The greatest amount of the nitride will be formed upon the decomposition of the γ-phase (75%), less by the β-phase (40%) and the least - by the decompositions of the β'-phase (20%). An X-ray diffraction investigation showed that all these phases are zirconium oxynitrides of various compositions. Thus, the γ-phase has the composition Zr_2ON_2 and crystallizes into cubic body-centered lattice with a constant of a = 10.135 Å; the β-phase is rhombohedral with a = 6.246 Å, α = 99°35', its composition corresponds approximately to the formula $Zr_7O_8N_4$; the β'-phase is also rhombohedral and corresponds to the composition $Zr_7O_{11}N_2$.

Vanadium-oxygen-nitrogen [445]. Upon the thermal decomposition of ammonium metavanadate in a medium of nitrogen or ammonia, thinned with hydrogen, at temperatures of 500-1000°C vanadium oxynitride will be formed. The compositions of the oxynitrides agrees with the data of [67], where it was demonstrated that upon the decomposition of the metavanadate the compound $V_xN_yO_z$ will be formed with $0.9 < x < 1.14$; $0.94 < y < 0.98$; $0.02 < z < 0.04$

Niobium-oxygen-nitrogen. In work [443] part of the Nb-O-N system with the ratios (N, O)Nb $\leq$ 1 was investigated. Two ternary oxynitride phases were established: $NbN_{0.9}O_{0.1}$ with an NaCl structure (the lattice constant is a = 4.373-4.390 Å) and also $NbN_{0.6}O_{0.3}$ with a tetrohedrally deformed lattice of the NaCl type. The lattice constant varies from a = 4.370, c = 4.295 Å, c/a = 0.983 to a = = 4.386, c = 4.325 Å, c/a = 0.986. Other ternary phases were not detected.

An attempt to produce niobium oxynitrides by interacting niobium oxides with niobium nitrides or with other nitrogen-containing compounds of niobium did not yield positive results: in all cases the δ-NbN phase was formed with a very how oxygen content [910]. Niobium oxynitrides were obtained by treating Nb_2O_5 with ammonia at a temperature of 750-800°C. They all have the structure either of cubic δ-NbN, or hexagonal ε-NbN. The oxynitrides are characterized by low stability; they decompose upon heating to 1000°C (Table 112, [920]). Niobium oxynitrides have severe defectiveness in the niboium sublattice.

Table 112. Producing conditions and properties of niobium oxynitrides.

Composition	Temperature, °C	Reaction time, h	Structural type	Pycnometric density g/cm³
$Nb_{0,76}N_{0,82}O_{0,19}$	750	482	δ-NbN	6,86
$Nb_{0,70}N_{0,76}O_{0,24}$	800	12	δ-NbN	6,48
$Nb_{0,69}N_{0,75}O_{0,25}$	800	20	δ-NbN	6,42
$Nb_{0,82}N_{0,81}O_{0,19}$	800	625	ε-NbN	7,27

In [1062, 1081] the solubility of mixtures of nitrogen and oxygen in niobium was investigated. Upon dissolution the electrical resistance of niobium increases (by 4.1 μΩ/cm for each at. % of dissolved gas); the specific magnetic susceptibility decreases; the microhardness increases (from 64 kg/mm^2 for pure niobium to 525 kg/mm^2 with a nitrogen and oxygen content of 4.5 at. %) where the effect of the dissolved nitrogen of the hardness of niobium is greater than oxygen.

Tantalum-oxygen-nitrogen [546]. In the system four oxynitrides were detected with the compositions: $TaN_{0.90}O_{0.10}$ (the structure is similar to ε-TaN, a = 10.34; c = 5.802 Å; c/a = 0.561), $TaN_{0,75}O_{0,25}$ (it has the structure of the δ-phase of the Ta-N system, the lattice constant is: a = 5.988; c = 2.879 Å; c/a = 0.481), $TaN_{0,65}O_{0,35}$ (the superlattice is of the type of that for the δ-TaN phase, the lattice constant is: a = 10.34, c = 2.864 Å, c/a = 0.277) and

$TaN_{\sim 0,50}O_{\sim 0,50}$. (a hexagonal lattice with the constants: a = 5.939; c = 2.866 Å; c/a = 0.483). The color of the oxynitrides varies from black for $TaN_{\sim 0,90}O_{\sim 0,10}$ to reddish for $TaN_{\sim 0,50}O_{\sim 0,50}$. The interatomic distances differ comparatively little from the interatomic distances of TaN.

Buslayev [979] from tantalum nitride-chloride Ta_2N_3Cl produced tantalum oxynitride TaON, the individuality of which was confirmed by an investigation of its infrared-spectrum. This substance is stable with respect to inorganic acids and alkalis; it is decomposed by a mixture of hydrofluoric and sulfuric acids. In an inert medium at least up to 900°C it is stable; it is assumed that at 840°C its polymorphic transformation occurs with packing of the crystal lattice and a change in its color from red to green. The TaON in both variants is diamagnetic.

The existence of this compound was confirmed by the works [980, 986], where it was obtained, by acting ammonia with tantalum pentoxide, at a temperature of about 800°C. This compound is an intermediate product of the nitridation of tantalum pentoxide with the producing finally of tantalum nitride Ta_3N_5. According to preliminary data the crystal structure of TaON is analogous to the structure of baddeleyite (the monoclinic variant ZrO_2) with lattice constants of: a = 5.145; b = 5.207; c = 5.311; β = 99.23°.

Chromium-oxygen-nitrogen [444]. By acting a stream of ammonia and hydrogen on chromium hydroxide or an oxalate complex of chromium $(NH_4)_3|Cr(C_2O_4)|3H_2O$ at 600-1000°C chromium oxynitride CrN_xO_y will be formed, where $0.8 < x < 0.9$; $0.1 < y < 0.2$.

Tungsten-oxygen-nitrogen [919]. Tungsten forms oxynitrides by interacting WO_3 with ammonia at 700°C, the composition of which can be described by the general formula $W_xN_yO_{1-y}$ with $x \approx y \approx 0.62$.

Zirconium-tantalum-oxygen-nitrogen [900]. The existence of a quaternary nitride has been established with the composition ZrTaON,

having a hexagonal structure with constants of: a = 3.645; c = = 3.881 Å, c/a = 1.065. The calculated density is 11.24 g/cm^3.

Thorium-oxygen-nitrogen [968]. The existence in this system of the compound Th_2N_2O is indicated, obtained by heating of pressed mixtures 3ThN + ThO_2 at a nitrogen pressure of 2 at. at a temperature of 1700°C. This compound crystallizes into a rhombohedral lattice with parameters of: a = 9.398; c = 23.78 Å (the parameters of the corresponding hexagonal lattice are: a = 3.871; c = 27.385 Å); the density is 10.55 g/cm^3.

Uranium-carbon-oxygen-nitrogen [949]. With the reduction of UO_2 with carbon in a nitrogen medium due to the solubility of oxygen in the carbonitride uranium oxycarbonitride $UN_{1-x-y}C_xO_y$ will be formed which is closer to a chemical individuum than to a solid solution. The solubility O_2 in the carbonitride depends on the carbon concentration and the partial pressures of the nitrogen and the carbon monoxide. By thermodynamic calculation the boundary of the region of homogeneity of the oxycarbonitride and the maximum content of oxygen impurity were established; the result of the calculation are checked experimentally. For example, with the heating of the carbonitride with x = 0.43 in an argon medium with $P_{N_2} = 10^{-5}$ and $P_{CO} = 3.5 \cdot 10^{-6}$ at. the concentration of the oxygen impurity corresponds to y = 0.006. Concerning uranium oxynitrides see [1083].

5. Metal-Halogen-Nitrogen Systems

Barium-halogen-nitrogen [442]. The existence of ternary compounds in the Ba_3N_2-$BaCl_2$, Ba_3N_2-$BaBr_2$, Ba_3N_2-BaJ_2 systems has been established, having the compositions Ba_2NCl, Ba_2NBr, Ba_6NJ_9. Their structure has not been clearly established; the heats of formation are respectively equal to: 44.4; 46.3; 53.5 kcal/mole. These compounds melt congruently at respective temperatures of 965, 918 and 810°C.

Titanium (zirconium)-iodine (chlorine, bromine)-nitrogen. In

the Ti-J-N [Translator's note: the letter J is being used for iodine] system compound TiJN was established [914], which readily hydrolyzes and is thermally unstable (it is the least stable of all the examined compounds). Its structure is of the type EO_5; its space group is D_2^{13}(FeOCl); they are described in greater detail below.

In the zirconium-iodine-nitrogen system the compound ZrNJ will be formed, having the appearance of elongated, orange-colored leaflets with a length of about $3 \cdot 10^{-3}$ cm and a width of $0.5 \cdot 10^{-3}$ cm. The crystal lattice is rhombic of the EO_5 type (the type FeOCl) with constants of: a = 4.114; b = 3.724; c = 9.431 Å; the number of formula units per cell is 2; the X-ray density is 5.34 g/cm^3. It is stable in the absence of moisture [424]. The structure is the typical layer-like with the order of layers along the z axis: NZrJ/JZrNNZr/JJZrN. The distance between both J layers is relatively great (3.12 Å), and between the N layers - small (0.43 Å). It is assumed that the nitrogen occupies an intermediate position between, on the one hand, an anion of the layer-like structure, with the other - component parts of the grouping $(ZrNNZr)_{\infty}^{2+}$.

The existence of the connections ZrNCl, ZrNBr, TiNCl and TiNBr has also been established [914], which forms two variants each, where all the α-variants have the above described structural type EO_5; a great part of these compounds has low chemical and thermal stability, except β-ZrNCl and β-ZrNBr, which are distinguished by comparatively high stability in a chemical regard and upon being heated. The investigation of the structure of these two compounds showed [915] that they have a hexagonal layer-like structure (layers xZrNNZrx) with the constants: β-ZrNCl a = 2.08; c = 9.23; β-ZrNBr a = 2.10; c = 9.75 Å.

6. Metal-Silicon-Nitrogen Systems

Lithium-silicon (germanium, titanium)-nitrogen [425]. By heating mixtures of binary nitrides at a temperature of 850-1300°C in a metallic bomb under conditions, excluding the admission of

moisture and oxygen (in a nitrogen or ammonia medium, accelerating the formation reaction of ternary nitrides), the nitrides Li_5SiN_3. Li_5TiN_3 and Li_5GeN_3 were observed. All these nitrides have a cubic structure with constants of lattice respectively of 9.44; 9.70; 9.61 Å (the space group is La3). The nitrides have a bright color, they hydrolyze readily; they dissolve in dilute acids; they are thermally stable (Li_5SiN_3 metals above 1300°C).

Beryllium-silicon-nitrogen [907]. With the sintering in an ammonia medium of mixtures of Be_3N_2 and Si_3N_4, taken in stoichiometric ratios, at 1750-1800°C in crucibles of boron nitride a compound of the composition $BeSiN_2$ will be formed which is reminiscent of aluminum nitride. It has a hexagonal structure with lattice constants of: a = 2.87; c = 4.67 Å; c/a = 1.62; the X-ray density is 3.24; the pycnometric density is 3.12 g/cm^3.

A subsequent investigation of the producing conditions and the properties of the compound $BeSiN_2$ was carried out in [1035], where the producing conditions, established by Rabenau and Eckerlin in [907] the above-indicated lattice constants were confirmed. It was demonstrated that samples $BeSiN_2$ are stable when heated in air to 900°C; at 1000°C oxidation is intensified, and rate of the oxidation decreases with time. The end product of oxidation is the silicate Be_3SiO_4 (phenacite). The compound is thermally stable when heated to 2000°C; at higher temperatures it decomposes (in a nitrogen-hydrogen mixture medium); it is also assumed that at 1950°C it sublimates without decomposing.

Magnesium-silicon-nitrogen [1043]. In this system the compound $MgSiN_2$ will be formed, produced by the joint heating of magnesium and silicon nitrides at 1200°C in a nitrogen medium. The ternary nitride is nonhygroscopic; it is insoluble in alkalis in the cold, and also in dilute and concentrated mineral acids; it slowly reacts only with 40% HF and with heated alkaline solutions. In the presence of oxygen at 1250°C it oxidizes completely, being converted into magnesium metasilicate.

Calcium-silicon-nitrogen [938]. In this system the existence of three compounds has been detected: $CaSiN_2$ (phase I), $Ca_5Si_2N_6$ (phase II) and Ca_4SiN_4 (phase III), produced by interacting Ca_3N_2 and Si_3N_4, or the complex nitride (phase II) with calcium or silicon nitrides

$$5Ca_3N_2 + 2Si_3N_4 = 3Ca_5Si_2N_6 \text{ (at} \sim 600°C),$$
$$Ca_5Si_2N_6 + Si_3N_4 = 5CaSiN_2 \text{ (at} \sim 800°C),$$
$$Ca_5Si_2N_6 + Ca_3N_2 = 2Ca_4SiN_4 \text{ (at} \sim 800°C).$$

Phase II can also be formed by interacting phases I and III at a temperature of 1180°C for 24 h

$$CaSiN_2 + Ca_4SiN_4 = Ca_5Si_2N_6,$$

i.e., it is the stablest.

In work [983] a tentative phase diagram of the Ca_3N_2-Si_3N_4 system was plotted showing region of the location of the three indicated phases, and also of the solid solution of Si_3N_4 in Ca_3N_2. The solubility of silicon nitride in calcium nitride at a temperature of 1050°C is 1.12 molar %.

Transition metal-silicon-nitrogen [314, 928, 929]. Upon interacting a sample, containing 62% Ti and 35% Si, with nitrogen TiN will be formed. No other phases in the Ti-Si-N system have been detected. In the Zr-Si-N system upon heating zirconium with Si_3N_4 in a crucible of ZrO_2 in the presence of nitrogen at a temperature of 1800°C there appears along with elementary silicon a hexagonal phase of indefinite composition with constants of: a = 7.603; c = 2.906 Å, which, obviously, is a ternary compound of zirconium with silicon and nitrogen. In investigatin the Ta-Si-N system samples were prepared by sintering mixtures of Si_3N_4 with Ta_2N or $TaSi_2$. The heating of these samples 1327°C showed that $TaSi_2$ is unstable in the presence of nitrogen and interacts with it, forming the ternary phase $Ta_{5-x}Si_{3-y}N_z$. The Ta_2N is in equilibrium with this ternary phase and, probably, TaN also.

According to the results of an X-ray analysis a preliminary diagram of the system (Fig. 148) was plotted. The Nb-Si-N system was plotted analogously; the ternary compound $Nb_{5-x}Si_{3-y}N_z$ forms in it. Both have broad regions of homogeneity.

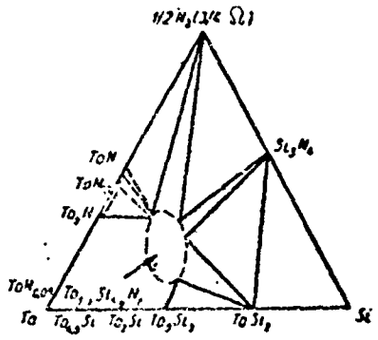

Fig. 148. Phases of the ternary Ta-Si-N system.

In the cerium-silicon-nitrogen system ternary compounds were not detected.

Iron-silicon-nitrogen. The effect of small quantities of silicon on the solubility of nitrogen in α- and γ-iron can be expressed by the equation $\lg S_x/S_0 = -Ax$, where S_x and S_0 is the solubility respectively in iron-silicon alloy and in pure iron, x is atomic content of silicon. Value A decreases with an increase in temperature and is greater for the α-phase than for the γ-phase [944]. In work [945] it was established that upon alloying alloys of the Fe-Si system with nitrogen the silicon nitride Si_3N_4 will be formed. Silicon lowers the solubility of nitrogen both in α- and also in γ-iron.

7. Nonmetal-Nonmetal-Nitrogen Systems

The silicon-carbon-nitrogen system is one of the most completely studied systems [873, 874, 876, 931, 1036], in which in spite of voluminous research, it was not possible to detect ternary nitrides: the alloys of this system consist of silicon nitride and silicon carbide.

In the aluminum-boron-nitrogen system the existence of a ternary compound is assumed [884, 932]. An investigation of alloys, produced by the nitridation of mixtures of AlN + B and BN + Al (at temperatures respectively of 1600-2000°C and 1200-1400°C it was demonstrated that along with the phases which are the original components or products of their nitridation a phase of high hardness appears (of the order of 5000 kg/mm^2), and the materials themselves - the products of nitridation - have a high electrical resistance.

In work [898] a refractory material of the boron-carbon-nitrogen system was described, consisting of 80% boron nitride and 20% boron carbide and obtained by the hot pressing of mixtures of these components. Subsequently, in work [771] the production of analogous materials was proposed by nitridation boron carbide, and it was established that they fundamentally differ in properties from mechanical mixtures of boron nitride and boron carbide. In connection with this the assumption was made that in this a ternary compound will be formed, close in structure to hexagonal boron nitride, but in contrast to it having an increased statistical weight of sp^3-configurations of boron, carbon and nitrogen atoms which gives to it increases properties (high stability in a vacuum, dielectric properties at high temperatures, chemical stability). It is assumed that at high pressures and increased temperatures this compound should acquire a diamond-like structure, analogous to boron nitride and graphite.

In work [974], dedicated to the investigation of the conditions for preparing of articles of boron carbide, in particular, the lubricating action of additives of boron nitride to powdered boron carbide during hot pressing was investigated. It was demonstrated that the greatest density is obtained by the hot pressing of equimolar mixtures (B_4C:BN = 1:1) and reaches 97%. It is possible to assume that this is connected with the formation in this composition in the process of hot pressing of a considerable quantity of the above-indicated ternary compound.

Sulfur-fluorine-nitrogen [926]. In the system the compound $S_4F_4N_4$ was detected with a melting point of 153°C (it decomposes upon smelting); its density is 2.326 g/cm^3; its dielectric constant is $\varepsilon = 2.257$; its dipole moment is $\mu = 0$. It crystallizes in a hexagonal system; its space group is D^4_{2d}, its lattice constant is: $a = 9.2$; $c = 4.3$ Å. It is hydrolyzed in a warm dilute NaOH solution. The gaseous compound SF_2N_2 is also konwn with a melting point of 108°C, a boiling point of − 11°C, a density of 1.57 g/cm^2.

Sulfur-oxygen-nitrogen [927]. Upon reacting S_4N_4 with a mixture of SO_2 and $SOCl_2$ a solid phase of yellow-colored $S_3N_2O_2$ will be formed.

C H A P T E R X

NITRIDE COATINGS

Many nitrides, simultaneously possessing high hardness and wear resistance, are finding broad application for the creation of protective coatings on metals, alloys, nonmetallic substances, graphite.

Especially broadly developed is the nitridation of steels, as one of the basic directions in chemical-heat treating [741, 742]. Nitridation steels possess high surface hardness, increased fatigue-limit, corrosional and cavitational stability, and also high wear resistance. Even more widespread is the simultaneous saturation of a steel surface with carbon and nitrogen from a gaseous medium (carbonitriding) and from molten cyanogen baths (cyaniding).

These increased properties are possessed by nitrided and carbonitrided steels thanks to the presence in the surface layer of nitrogen in the form of nitrides or carbonitrides. Important also is the increase in the resistance of steels during welding in nitrogen to intercrystalline corrosion [761], and the increase in their fatigue and corrosion-fatigue strength [955].

The problem of nitridation, cyaniding, carbonitriding steels is covered by extensive literature, a survey of which is given in the above-indicated and other monographs on the chemical-heat treating of steels (for example, [743, 744, 1032]).

The nitridation of iron with the corresponding investigation of the mechanism and the kinetics of the formation of the diffusion layer and phase transformations is covered by a large series of works, carried out under the general leadership of V. G. Permyakov, for example, the important work [973].

In this work we will dwell only on questions of creating coatings of the nitride type on refractory metals and alloys [745, 747].

The formation by nitridation of simple or complex solid solutions of nitrogen or chemical compounds - of nitrides is possible, usually ensuring the highest properties of the coatings.

The nitridation of titanium with nitrogen and ammonia leads with the use of ammonia to diffusion layers of great depths and to their greater hardness, however the simultaneously occurring diffusion of hydrogen causes their increased fragility [748], obviously, caused by the increase in the rigidity of the bonds by the introduction of hydrogen into the vacancies of the nitride lattice and the formation as a result of hydride-nitride phases, which was mentioned in Chapter II.

Although hydrogen can to a considerable degree be removed by vacuum treating, nevertheless the nitridation method with the use of ammonia is technologically and economically inexpedient.

The thickness and the properties of the layers on the titanium after the nitridation in a nitrogen medium are given, according to [748], in Table 113.

When nitridation with ammonia in the same temperature range elongation drops to 2%, and resilience to 0.3-0.5 cm^2. As can be seen from the given data, the depth of the layer does not obey the parabolic law of increase with nitridation time. Analogous results were obtained by A. N. Minkevich with his colleagues [749], who nitrited pure titanium and titanium alloyed with chromium and tungsten in ammonia at temperatures of 850-1050°C. It was discovered

that with small expenditures of ammonia the layer in certain cases is deeper than with large expenditures, and with an increase in temperature the optimum expenditure of ammonia, necessary for the production of a layer of maximum depth, is increased. The layer of depth varied not according to a curve, close to a parabola, but according to a curve with a maximum. An X-ray investigation of the layer showed that at the nitridation temperature 1050°C the layer is a solid solution of titanium nitride and hydride (and TiO - with the use of insufficiently oxygen-purified ammonia). At a temperature of 950°C only a solid solution of nitrogen and hydrogen in the titanium was detected. The nitridation of titanium in ammonia increases its wear resistance by tens of times, however it lowers the strength and plasticity, especially if process is carried out at high temperatures and with protracted exposures.

Table 113. The effect of the parameters of the diffusion treating of titanium with nitrogen on the properties of the nitrited samples.

Temperature, °C	Time, h	Depth of layer, μ	Hardness at the surface H_V, kg/mm^2	Hardness at a depth of 100 H_V, kg/mm^2	Proportional limit kg/mm^2	Ultimate tensile strength kg/mm^2	Elongation, %	Resilience, kg/mm^2
700	8	25	1132	250	29.0	37.8	36.5	22.8
	16	42	1206	360	26.0	36.4	45	27.6
	24	33	1332	285	23.5	37.3	45	26.0
	48	35	1246	445	27.0	36.6	48.5	25.4
800	8	13	1003	205	26.0	36.7	43.0	25.1
	16	40	1333	325	26.4	36.4	45.0	21.1
	24	25	1520	280	24.5	39.5	45.0	26.8
	48	44	1426	360	26.0	37.4	39.5	23.5
900	8	53	1500	375	36.0	41.7	36.5	17.1
	16	61	1500	470	22.5	46.7	25.0	11.0
	24	76	1500	500	39.0	47.7	30.0	10.5
	48	31	1500	390	43.5	48.1	43.5	9.0

The alloying of titanium with tungsten leads to a sharp decrease in the depth of the nitrited layer. The titanium alloy with 5% r after nitridation reveals an increase in the wear resistance of

40-170 times (depending upon the conditions of saturation) as compared to non-nitrided industrial titanium. Inasmuch as nitridation in ammonia inevitably leads to considerable embrittlement of the articles, works were conducted on nitriding titanium in a mixture of argon with nitrogen [750-752]. With rarefaction the diffusion of nitrogen into titanium is accelerated which is due to the slower formation of the thin surface layer of TiN, inhibiting subsequent nitridation [752]. Nitridation in a medium with a proportional amount of nitrogen is connected with the difficulty of introducing a small amount of nitrogen, which it is necessary to add to the argon. The optimum content of nitrogen in the argon at 800°C is 1% [752]. The nitridation of titanium in a mixture of argon and nitrogen, which have first been subjected to thorough purification, is described in work [751]. An X-ray investigation of nitrited samples, carried out in this work, shows that the surface layer with a nitrogen content in the mixture with argon of more than 0.5% consists of TiN and TiN_x, where $x < 1$.

A crust consisting of nitrides prevents the diffusion of nitrogen into the depth of the metal, and thereby the thickness of the overall saturation of the surface layer with nitrogen is decreased. A decrease in the nitrogen concentration of up to 0.5% and less leads to the formation on the surface of a solid solution of nitrogen in Ti with inclusions of TiN and to the gradual transition to a pure solid solution of nitrogen in Ti. At a partial nitrogen pressure of 0.005-0.04 at and upon nitriding for 20 h at a temperature of 850°C it is possible to obtain a surface layer without the formation of titanium nitride. With greater exposure times, temperatures and partial pressures of nitrogen mixed with argon on the titanium there is always formed a thin layer of titanium nitride. The alloying with aluminum accelerates the diffusion of nitrogen into the titanium, increasing the depth of the diffusion layer, and manganese, tin, and especially silicon act in the opposite direction (Table 114).

Table 114. The effect of alloying of titanium on the depth of diffusion of nitrogen, the increase in weight of the samples of the microhardness distribution at 850°C.

Alloying element	Content of the alloying element, %	The presence of a nitride layer (according to microhardness and color)	Microhardness kg/mm^2, at a depth of 0.01 mm with a load of 100 g	Layer depth, μ	Increase in weight of samples, mg/cm^2 of surface	Exposure, h
Aluminum	1.74	No	824	50	0.92	4
	3.00	"	1000	56	0.95	4
	3.75	"	1000	50	0.85	4
	5.00	"	1100	48	0.73	4
	5.00	Yes	1200	120	-	24
Manganese	1.35	No	824	27	0.72	4
	2.45	"	1000	-	0.71	4
	3.76	"	1100	28	0.70	4
	6.54	Yes	1200	25	0.70	4
	6.54	-	1500	68	-	24
Silicon	0.66	No	1100	20	0.52	4
	1.62	"	1100	18	0.46	4
	1.62	Yes	1200	65	-	24
Tin	0.86	No	824	28	0.53	4
	1.58	"	824	24	0.74	4
	1.58	Yes	1100	83	-	24
Titanium iodide	-	No	824	25	0.82	4
	-	Yes	1200	90	1.05	24

The process of titanium nitridation in a stream of pure nitrogen at a temperature of 700-1050°C for a period of up to 10 h was studied in [753]. It was discovered that a noticeable increase in weight began at 800°C and followed the parabolic law up to 1000°C. It was established by the electron diffraction method that after nitriding at 800°C and higher the nitride TiN will be formed in the surface layer. An increase in hardness was slightly noticeable at 800°C, however at a temperature of more than 900°C the thickness and the hardness of the layer increases progressively with the time of nitridation.

Opinions about the benefit of nitriding at low partial nitrogen pressures and nitriding with pure nitrogen differ which is due to the various problems in nitriding. In certain cases it is necessary to ensure a nitridation layer of great depth, not bringing it to the state of a nitride, in others - to preserve the properties of the basic mass of the titanium component, increasing only its surface wear, corrosion resistance and hardness. The latter cases, as a rule, predominate [754-756].

The authors [754] nitrided titanium at 850°C for 16-80 h for the purpose of increasing its wear resistance, corrosion resistance and mechanical properties. Nitrited titanium worked satisfactorily without lubricating paired with cast pig iron, hard chromium coatings and non-nitrided titanium. When working with lubrication good results were obtained paired with bronze, carbon and low-alloy steel, bakelite, chrome-plated surfaces. Nitrided titanium showed high corrosion resistance in heated hydrochloric, sulfuric, phosphoric, nitric, hydrofluoric and other acids. Nitridation does not substantially effect the mechanical properties of titanium.

In work [755] samples of commercial titanium and heat-resistant titanium alloy with 6% Al and 4% V were subjected to nitridation in purified nitrogen at 980°C for 4-168 h. On commercial titanium the nitrided layer was considerably thicker than on the alloy of titanium with aluminum and vanadium, and its hardness attained 1650 H_V. It was noted that the values of the resilience of nitrided and non-nitrided titanium almost did not differ, when for the alloy they were considerably lower. This is connected with the presence in the nitrided alloy of nitrided grains, located at an angle of 45° to the surface and widespread to a great depth. Being, apparently, concentrates of stresses, they caused a considerable fall in resilience. A variation in the thickness of the nitrided layer on commercial titanium occurred with time like a parabola; the thickness was after 168 h of nitridation 0.2 mm.

An investigation of the process of nitriding titanium and its alloys in pure nitrogen was also conducted in work [756]. The optimum nitriding conditions were saturation at a temperature of 950°C for 24-30 h and a nitrogen feed rate of 0.12-0.15 ℓ/min. At lower temperatures the diffusion of nitrogen occurs slowly, at higher temperatures the fragility of the layer and the metal itself increases intensely. Under the indicated optimum conditions of nitridation a layer with a depth of 80 μ with a surface hardness of H_V = 780-850 kg/mm^2 increases on the samples of forged VT1 titanium. The nitrided layer consisted of several zones. On the surface a golden TiN film with a thickness of tenths of micron was formed above it a zone with a thickness of 8-10 μ with a nitrogen content of 10-12% was disposed, which consisted, apparently, of titanium nitride in the lower region of its homogeneity. After the nitride zone the greatest zone followed with a depth (60-80 μ) with a gradually diminishing microhardness (from 1300 to 700 kg/mm^2) with a content of from 4 to 1.5% N. This zone is α-Ti with an increase in the lattice parameter. An investigation of the mechanical properties of the nitrided samples, which had been subjected to a different additional treatment, showed (Table 115) that annealing in a vacuum at 800°C decreases the fragility of the layer and increases the characteristics of plasticity by 10-15%. In work [756] it is assumed that the main cause of the decrease (by 25-30%) in the plasticity of the titanium after nitridation is the increase in the grain as a result of prolonged high-temperature heating. Another cause of the reduction in plasticity is the deep penetration of the nitrogen into the titanium (with an increase in the depth of the photographed layer the plasticity of the titanium increases).

An investigation of the effect of alloying titanium with various elements showed that 2-2.5% Al, up to 2% Si and 1.5% Mn cause an increase in the depth of the nitrided layer. With a greater content of these elements the depth of the layer decreases. Chromium and iron reduce the depth of the nitrided layer independently of their content in the alloy. In this work the nitridation of certain ternary alloys of titanium was tested; it was established that alloys of grades VT2, VT3, VT5, and VT6 nitride more poorly than alloy VT1.

Table 115. The effect of nitridation and additional treatment after nitridation on the mechanical properties of the samples of VT1 alloy.

Treatment	$\sigma_в$ kg/mm^2	δ, %	ψ, %	a_k, kgm/cm^2
Original alloy, annealed in a vacuum at 800°C, 2 h	45.1	33.1	65.2	14.8
Nitridation, 950°C, 30 h (the nitrided layer was not photographed)	55.5	15.1	39.2	5.3
The same (the layer was photographed at a depth of 0.5 mm)	51.0	20.1	53.9	7.6
The same (the layer was photographed at a depth of 1 mm)	48.2	23.2	54.2	9.7
The same (the layer was photographed at a depth of 1.5 mm)	-	-	-	12.0
Nitridation at 950°C, 3 h + annealing in a vacuum at 800°C, 2 h, the pressure is $3 \cdot 10^{-4}$ mm Hg (the nitrided layer was not photographed)	54.2	19.4	35.0	10.6

According to [1064], with the nitridation of titanium, alloyed with Al, Cu and Sn, two nitrides are detected in the nitrided layer - the external layer consists of the fine-grained nitride TiN, and the following - of the lower nitride of the composition $Ti_{2.12-2.36}N$, forming a coarse-grained structure. The formation of these two layers was detected, in particular, upon the nitridation of the VT5 alloy for 30 h at 960°C in a stream of purified nitrogen.

Advantages of nitriding with the use of the heating of the articles with the streams of high frequency are shown in [757]. Upon nitridation VT4 and VT6 in this way (at a nitrogen pressure in the chamber of 40-50 mm Hg), a temperature of 1100°C for 20 min a layer was obtained with a thickness of 30 μ with a microhardness

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of 2000 kg/mm^2. Abrasion testing paired with tempered U12A steel under conditions of dry friction practically did rot show a change (wear) in the nitrided samples. The heat resistance of the nitrided samples in air at 1000°C was four times higher than the heat resistance of non-nitrided samples.

The advantages of induction heating with streams of high frequency during nitridation consist in the acceleration of the formation of the diffusion layer and in the possibility of increasing the temperature of only the surface layer, not affecting the basic mass of the metal, the optimum structures and the properties of which were established by the preliminary treatment [760].

The nitridation of titanium, apparently, most substantially fixes the surface properties of the articles in a technical regard, having a number of advantages over carburizing by various methods [758].

In work [237] the method of applying titanium nitride, in particular, to a molybdenum surface by the gas transport method was described, based on the decomposition of titanium nitride by HCl vapors

$$TiN + 4HCl = TiCl_{4(газ)} + 0{,}5\,N_2,$$

with the subsequent transfer of titanium chloride to molybdenum and its transformation to a nitride due to its reaction with a nitrogen-hydrogen mixture and its deposition on the molybdenum. Thin layers of the nitride hold firmly to the molybdenum, thick layers - crack.

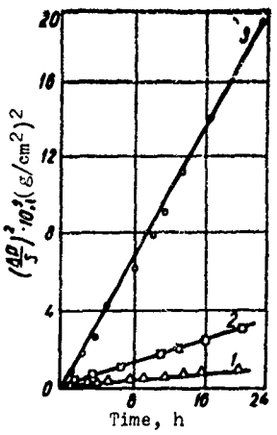
Along with the method of gas transport reactions for nitriding various electromethods are beginning to be employed of which it is necessary to mention ionic nitriding, consisting in the excitation of the glow discharge in a vacuum, containing nitrogen atoms and ions between the cathode (component) and the anode. Then a stream of ions of nitrogen is directed toward the surface of the component; they accomplish nitridation rapidly, furthermore, heating the surface as a result of collisions against the cathode [759].

Nitridation is substantially intensified with the use of ultrasonics [762].

An investigation of reaction diffusion in metal-complex gas systems is covered by the work of the school of V. I. Arkharov [763-765]. V. I. Konev [763] investigated the structure and the properties of carbonitrided coatings on chromium. The samples after being chromium-plated were treated in a mixture of gasoline with nitrogen at a temperature of 700-1100°C. An X-ray analysis and a metallographic investigation of the coating showed that its external layer consists of Cr_3C_2, the middle layer - of Cr_7C_3, and the internal layer, adjacent to the metallic core, - of Cr_2N. If the chrome layer had a textured building, then the layer, consisting of chromium nitride, also possessed a texture, obeying the principle of orientational structural-dimensional correspondence. As follows from Fig. 149, reaction diffusion in the Cr-N, Cr-C, Cr-C-N systems obeys the parabolic law, where the diffusion mobility of the nitrogen atoms is much higher than the carbon atoms [1111].

Tests for acid and wear resistance showed that carbonitrided coatings on chromium are not inferior in properties to carburized coatings. Identical results were also given by a test of these coatings for resistance to oxidation which is explained by the fact that in both cases the upper layer of the coating consists of chromium carbides. A carbonitrided layer will be formed as a result of the diffusion of nitrogen and carbon atoms through corresponding layers of chromium carbides and chromium nitride; a noticeable counter diffusion of chromium atoms was not observed. The reaction front of nitrogen with chromium is on the interphase boundary of $Cr-Cr_2N$, and carbon with chromium - on the boundary $Cr_2N-Cr_7C_3$. The clear boundary between Cr_2N and Cr_7C_3 indicates the limited solubility of these phases.

In work [334] the conditions of applying nitride coatings on chromium in the temperature interval of 1000-1300°C were also investigated.



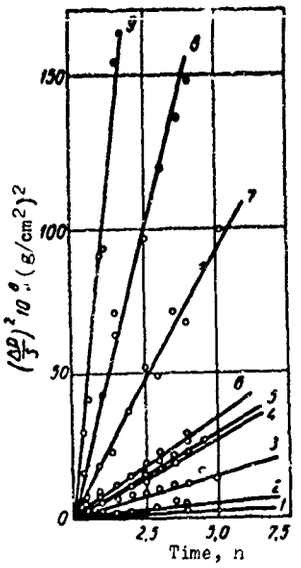


Fig. 149. Fig. 150.

Fig. 149. Dependence of the increase in weight of the samples of chromium at 1100°C, on the duration of the carburizing processes (1), carbonitriding (2) and nitridation (3).

Fig. 150. The dependence of the increase in weight of the Mo samples in an ammonia medium on time at temperatures of: 1 - 700; 2 - 750; 3 - 820; 4 - 880; 5 - 900; 6 - 940; 7 - 1000; 8 - 1050; 9 - 1120°C.

The nitridation, carburizing and carbonitriding of molybdenum were investigated [764]. Saturation with nitrogen was carried out in medium of ammonia and molecular nitrogen at temperatures respectively of 700-1150° and 800-1200°C, where in the second case the interaction of molybdenum with nitrogen at atmospheric pressure was not detected. In an ammonia medium the saturation of molybdenum with nitrogen obeys the parabolic law in the whole temperature range (Fig. 150). Up to a temperature of 940°C two layers will be formed on the molybdenum surface; the external MoN and the internal Mo_2N. At a temperature above 940°C only the phase Mo_2N is stable, at a temperature above 1150°C it also vanishes. The joint saturation of the molybdenum surface with nitrogen and carbon was carried as well as of chromium in [763], only the nitrogen was replaced by ammonia. The formation of a diffusion layer, consisting of molybdenum carbonitride with a Mo_2C lattice, was observed at a temperature of 1000-1200°C and it obeyed the parabolic law (Fig. 151). An

investigation of the kinetics of the formation of diffusion layers in molybdenum-nitrogen, molybdenum-nitrogen-carbon and molybdenum-carbon systems shows that their growth proceeds due to the preferential diffusion of nitrogen and carbon through the reaction products to the metal, where the rate of nitridation of molybdenum is considerably higher than its carburizing rate, and the rate of the joint saturation with nitrogen and carbon has an intermediate value. The results of the X-ray and the metallographic investigations of the surface diffusion layers in the indicated systems are given in Table 116.

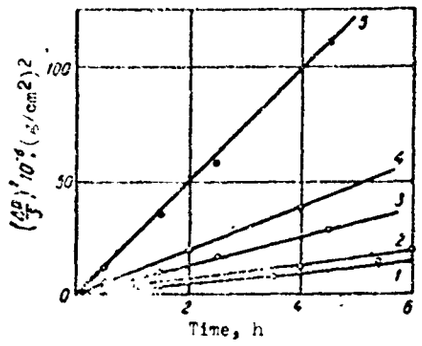


Fig. 151. The dependence of the increase in weight of Mo samples in a medium of gasoline and ammonia vapors on time at temperatures: 1 - 1000; 2 - 1050; 3 - 1100; 4 - 1150; 5 - 1200°C.

In works [956, 957] information is given about the doubling of the hardness of the molybdenum alloy with 1% Ti by treatment in nitrogen at temperatures of 1100-1500°C for 27 h. This increase in hardness is due to the formation of titanium nitride, dispersionally distributed in the molybdenum matrix. It is also indicated [956] that upon nitriding molybdenum alloy with 0.5% Ti the hardness increases from 290 to 660 H_V, and upon nitriding molybdenum alloy with 0.5% Ti and 0.08% Zr the hardness increases to 835-858 H_V.

Table 116. The results of nitriding, carburizing and carbonitriding molybdenum.

System	Temperature range, °C	Number of layers, revealed by metallographic investigation	Results of the X-ray phase analysis	Presence of texture
Mo-N	700-900	2	External layer - MoN Internal - Mo_2N	No
	940-1150	1	Mo_2N	"
	1150-1250	-	Mo	"
Mo-C	800-1200	1	Phase with an Mo_2C lattice	" (texture at 1200°C)
Mo-C-N	900-12[illegible]0	1	Phase with an Mo_2C lattice	No

An investigation of the nitridation of molybdenum (the molybdenum alloy TsM-2A 0.003% C; 0.09% Ti; 0.14% Zr) was carried out in [1051] various media (ammonia, dissociated ammonia, a mixture of nitrogen and 1% ammonia, a mixture of argon and 1% ammonia, rarefied (to 10^{-1} mm Hg) ammonia) at 700-1600°C for from 0.25 to 10 h. As a result it was established that during nitriding the dissolution of the nitrogen in molybdenum occurs first; then the nitrogen-poorest β-phase (Mo_3N) will be formed, then the nitrogen-richest phases Mo_2N and MoN (up to a temperature of 1000°C) or only the nitride MoN (at a nitridation temperature above 1000°C) which contradicts the data of [764] according to which the Mo_2N phase is stabler, and at temperatures above 1150°C neither of these phases will not be formed.

The nitrided layers on molybdenum obtained in [1051] possess high hardness (of the order of 2000 kg/mm^2) and high fragility (points 3-4 on the microfragility scale), where the volume changes, occurring during nitridation, cause high internal stresses, the

removal of which leads to the appearance of microscopic cracks. The heat resistance (measured by the resistance of plastic deformation upon testing for creep) is increased by 60-90% by the surface nitridation of molybdenum at 1000-1400°C. It was determined that this increase is attained under optimum nitriding conditions for sheet molybdenum (with a thickness of 1-1.5 mm) at 900-1000°C for 1 h.

The separate and joint diffusion of carbon and nitrogen into tungsten were studied in [765] (Table 117).

Table 117. The results of nitriding, carburizing, and carbonitriding of tungsten.

System	Range temperatures	Number of layers, detected by the metallographic analysis	The results of the X-ray phase analysis of the layers	The presence of the texture
W-N	1000-1100	2	External - WN, internal - W_2N	No
W-C	1000-1200	2	Internal - W_2C external - WC	"
W-C-N	1000-1200	2	External - with WC lattice, internal - with a W_2C lattice	"

From a comparison of the shapes of the kinetic curves (Fig. 152) it is possible to conclude that the presence of nitrogen inhibits the diffusion of carbon into the tungsten (for chromium and molybdenum the reverse phenomenon was observed). Inasmuch as during carburizing and during carbonitriding the partial pressure of carbon in the reaction space remained identical, the authors of the work [765] assume that the tungsten carbides forming in the diffusion zone contain dissolved nitrogen, which hampers the diffusion of the carbon atoms through the carbide phases further into the depth of the metal. The parabolic law of the increase in the thickness of the surface layer observed in all the systems testifies to the preferential

diffusion of nitrogen and carbon through the crystal lattices of the forming phases.

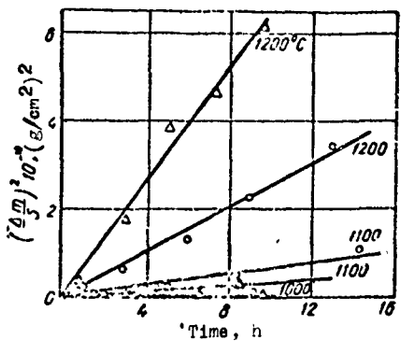


Fig. 152. The dependence of the square of the increase in weight of tungsten samples on time: Δ is the W-C system; O is the W-C-N system.

The authors [766] described the method of applying nitride coatings on titanium, zirconium and niobium by interacting halide connections of these metals with ammonia. As a result of this complex connections of various compositions will be formed, which decompose at high temperature, with the liberation of active metal and nitrogen atoms, diffusing into the surface being saturated. To apply a coating of titanium nitride it is recommended that an interaction reaction of $TiCl_4$ with NH_3 be carried out at temperatures of 900-1200°C. To avoid the liberation of the nitride particles in the free state the $TiCl_4$ and the NH_3 are introduced into the reaction zone separately, where the titanium chloride is in a stream of hydrogen.

The theory of the application of protective coatings of nitrides through a gas phase is covered in work [1065].

As was reported in [271], during the application of a nitride coating on magnesium (its alloy with 0.6% zirconium and others at a pressure of 30 at) relatively stable layers are formed preventing the magnesium from sublimating at increased temperatures.

Of great interest are nonmetallic nitride coverings on metals and nonmetals, in particular heat and corrosion resistant coatings of AlN [767], coatings of boron pyronitride and boron pyrocarbonite

[746], and also coatings of metal-like nitrides on nonmetals, for example, of titanium nitride on graphite [768].

According to [842], coatings of aluminum nitride on graphite were applied by the plasma spraying of aluminum on graphite with subsequent nitridation. The adhesion of the aluminum layer to the graphite is accomplished only as a result of mechanical fastening with subsequent nitridation at 1300°C for 0.5 h; the aluminum layer is completely converted into aluminum nitride and the layer fits tightly to the graphite substrate, being firmly held to it. The nitridation occurs especially qualitatively with the covering of the graphite component coated with aluminum with aluminum powder, which interacts with the oxide films on the aluminum layer with the elimination of the aluminum monooxide $Al_2O_3 + Al = 3AlO$.

CHAPTER XI

THE REGIONS OF THE APPLICATION OF NITRIDES

The variation within broad limits of the nature of chemical binding and the physical-chemical properties of nitrides assures for them very diverse fields of application. However the most developed at the present time is the use of refractory and electric insulating properties of certain nitrides - boron, silicon, aluminum, and also their complex compounds and various materials based on them.

Boron nitride. The high electric insulating properties, the resistance with respect to thermal shocks, the chemical stability, the strength at high temperatures, the good thermal conductivity, the stability in a vacuum, the great neutron-capture cross section in combination with good workability, and also the high refractory properties ensure the application of boron nitride and articles of it in various branches of technology. It is necessary to note expecially the use of boron nitride for the manufacture of protective insulating tubes for thermocouples, furnace accessories, pipes for muffle furnaces, transistor mountings, electron tube bases, crucibles, tubes and valves, devices for nuclear technology [628]. Of great value is the application of boron nitride for the manufacture of metal-wire components, electromagnetic pumps for pumping molten metals [896], channel linings MHD [magnetohydrodynamic] generators, certain devices for rocket technology. The use of the luminescent properties of boron nitride, alloyed with different impurities, is promising. Boron nitride has found real application as a thermoinsulator in high-frequency induction furnaces, since it is not heated by

induction currents even at high temperatures [769]. From it there are manufactured refractory coatings for molds and crucibles, refractory electrode holders for automatic welding; its application has been proposed for the manufacture of pouring lips of mixers and converters, however very high resistance of articles of boron nitride with respect to molten steel at temperatures higher than 1590°C was not detected [783]. Also promising is the use of boron nitride as a high-temperature lubricating material [770], for manufacturing light-load slider-type bearings. Its introduction into copper electrodes for the electroerosional treatment of metals sharply increases their relative stability. The comparatively low value of dielectric losses in the whole range up to ultrahigh frequencies make it possible to use boron nitride in the construction of dielectrics [773].

In chemical machine building the high resistance of boron nitride to the effect of many chemical reagents can be used, the resistance to abrasive wear - for the manufacture of nozzles of various atomizing apparatuses.

Pyrolytic boron nitride is used in rocket technology [713] as shielding material.

A material consisting of 80% BN and 20% B_4C [898], is resistant to acute and frequent thermal cyclings, chemically inert, durable and hard. From it there are manufactured plasma jets, facings for exhaust nozzles, rocket combustion chambers. By addition pore formers a porous material is obtained for filters as catalyst carriers, etc.

Boron carbonitride ($B_xN_yC_z$) also possesses high properties [771], having high resistance to vaporization in a vacuum, close to that of the carbides and borides of refractory metals, resistance to the effect of many molten metals, salts and slags, high electric insulating properties, plasmostability.

Boron carbonitride has a specific electrical resistance at 20°C of the order of 10^{14}-10^{15} Ω·cm; dropping at 1400°C to $5 \cdot 10^5$ Ω·cm,

and at 2000°C - to $2 \cdot 10^4$ Ω·cm; it possesses high thermal conductivity; it processes well mechanically [771]. It is characterized by high resistance to the action of molten borax at 1000°C. Crucibles of boron carbonitride are stable for 10-15 h in ferromanganese carbide, metallic manganese, manganese-silicon at temperatures of up to 2000°C [678], in molten iron-titanium concentrate and its reduction products at 1600°C [772], lithium plasma at 2000-2500°C [667], copper mattes and slags, nickel matte at 1250-1300°C [541].

Cubic boron nitride - borazon, possessing high hardness, is used for manufacturing various abrasive tools of this same type and purpose which are abrasive tools, made from diamond [774], and in the alloyed (with admixtures) form it can find application as a semiconductor [664], capable of being exploited at increased temperatures without a severe loss of properties.

The use of the luminophor properties of boron nitride, alloyed with various admixtures [653], especially carbon, is promising.

Not excluded is the possibility of using boron nitride as a rubber filler, especially of microporous rubber for industrial and everyday use.

Aluminum nitride. The known refractory properties of aluminum nitride - its stability in molten aluminum, tin, gallium, boron anhydride up to temperatures of 1300-2000°C [586] - ensure the prospects of its use as a material for bath linings, electrolyzers, reservoirs for high-temperature gallium thermometers. The electric insulating properties of aluminum nitride make it possible to use it for manufacturing tubes for shielding metallic thermocouples, and its resistance to acids - in chemical machine building. Especially promising is the manufacture of coatings of aluminum nitride on steels, graphite, various metallic and nonmetallic materials. In work [866] a refractory material is described consisting of aluminum nitride with 10-20% carbon and flurspar, which can be used up to 2300°C for lining glass foundry baths, and baths of the electrochemical industry.

Especially interesting and important is the role of aluminum nitride in steels and iron [563, 572, 867, 870-872]. It was determined that one of the causes of the brittle rupture of ingot steel is the separation of aluminum nitride on the boundaries of the austenitic grain [867] and that in the presence of aluminum nitride the magnetic characteristics of transformer steel are substantially reduced [563].

However it was recently demonstrated that aluminum nitride, which was usually considered to be a harmful component steel ensures under definite conditions and contents (up to 0.08% nitrogen in the form of dispersed nitride) simultaneously an increase in the strength, plasticity and an improvement in the weldability of steel [871]. Aluminum nitride is introduced into steel in the form of finely dispersed powder ($\sim$1 μ), during hardening of the ingot it is distributed evenly and prevents the growth of the grain during heating. The dimensions of the grains are very minute - from 8000 to 31,000 grains per 1 mm^2; with a content of 0.07% aluminun nitride the growth of grains is not observed even upon prolonged exposure at 1100°C. For low-carbon steels the best combination of strength properties and resilience at low temperatures is given by the introduction of 0.06-0.08% AlN, and for low-alloy steels - 0.04-0.06%. The weld-affected zone of a welded joint, appearing during welding and being a cause of embrittlement, almost does not appear in this steel.

It has been demonstrated that the introduction of aluminum nitride into aluminum and its cermet alloys sharply increases the elastic modulus and the thermal resistance. Alloys of the SAP [sintered aluminum powder] type will be formed in which the aluminum oxide is replaced by aluminum nitride [868]. There are certain prospects for the use of the semiconductor properties of alloyed aluminum nitride [614].

High electro-, thermo-insulational and refractory properties are possessed by materials, consisting of aluminum and boron nitrides and also of aluminum nitride with silicon carbide. For example, in [884] the properties of alloys of the B-Al-N system are described,

which possess high electrical resistance, dropping more slowly with temperature than boron and aluminum nitrides separately [1112, 1113].

Silicon nitride. The refractoriness, the high resistance to thermal shocks, the good heat resistance of up to 1200-1300°C is responsible for the application of silicon nitride in the composition of various heat-resistant materials, especially important (in a practical regard) properties are possessed by materials of SiC-Si_3N_4, in which the silicon nitride is a binder, binding the carborundum grains with each other [873-877]. According to [873], the porosity of these materials is 15-20%, the compressive strength limit at 20°C is about 20-24 kg/mm^2, with fracture at 1000°C - 1.9-2 kg/mm^2; the thermal conductivity at 850°C is equal to 8.3 kcal/m·h·deg, the coefficient of thermal expansion (20-1200°C) is $3.8 \cdot 10^{-6}$ deg^{-1}, the heat resistance from 1600°C is 7 water heating-cooling cycles. These same materials, but made according to the technology of [876], have $\sigma_{разр}$ = 2-4 kg/mm^2, $\sigma_{изг}$ = 4-7 kg/mm^2, $\sigma_{сж}$ = 22-38 (20°C); 22-40 (600°C); 27-40 (800°C) kg/mm^2. These materials can be used for manufacturing refrigerator scrubbers, operating with hot gases, the caps of nozzles for spraying chemically active liquids, mixers, resistant to corrosion, and also to the simultaneous action of solid components of suspensions and pulps, for the facings of chemical equipment, electric welding chambers under flux. In the latter case the lining of the chambers is held for 2 h under flux without any variations. Especially promising is the use of silicon carbide as a binder of silicon nitride for manufacturing of pump components for pumping molten aluminum [877], for manufacturing the linings of aluminum electrolyzers [878]. Such materials manifest high resistance to the action of copper and nickel matte and slags at 1250-1300°C; they interact weakly with molten basalt (1400°C), with chloride melts (700-1100°C)[541]. The material SiC-Si_3N_4 is resistant to the action of zinc and its vapors [897].

In work [879] the prospect of using the complex materials SiC + Si_3N_4 + $MoSi_2$ as emitters in the infrared region of the spectrum was demonstrated.

Cases of Si_3N_4 and the materials SiC + Si_3N_4 are used for shielding metallic thermocouples when measuring the temperature of fluoride melts in aluminum electrolyzers (the resistance was 100 h at 940-970°C) [880].

The high electrical resistance of Si_3N_4 makes its use promising in the composition of volume resistances, thermistors and in composition of heating electrodes of electric resistance furnaces [881].

The use of Si_3N_4 is recommended in the composition of heat-resistant alloys [882, 883].

The high hardness of silicon nitride make it possible to use it in the composition of abrasive materials. Thus, according to the patent [946], silicon powders or ferrosilicon with the addition of up to 50% SiC or without it are pressed for binding of glucose in the form of abrasive wheels, which are then roasted in a medium of nitrogen or ammonia at 1100-1600°C for 24-108 h, and abrasive articles are obtained, consisting of Si_3N_4:SiC = 2:1. It is also possible to use pastes of similar materials. The hardness of the abrasive is close to the hardness of SiC; with respect to the abrasive properties (when grinding cast iron, alloys of cobalt with chromium and tungsten, and also ruby) it is superior to carborundum and electrocorundum.

Of great practical interest are materials, consisting of silicon nitride with magnesium and aluminum oxides [1040]. The materials MgO-Si_3N_4 [1114] possess a flexural strength limit of 12-14 kg/mm^2, a compressive strength limit of 30-35 kg/mm^2; the increase in weight upon oxidation at 1200°C is 3-6 mg/cm^2; the electrical resistance is 10^{10}-10^{13} Ω·cm; the thermal resistance at 1500-20°C - 20-30 thermal cycles; they are resistant to the effect of borax and zinc melts. The materials Al_2O_3-Si_3N_4 [1115] have a flexural strength limit of 6-7 kg/mm^2, a compressive strength limit of 16-18 kg/mm^2, the increase in weight upon oxidation at 1200°C is 2-5 mg/cm^2, the electrical resistance is 10^9-10^{11} Ω·cm, the thermal resistance is 30-35 water thermal cycles (1500-20°C).

In [1058, 1116, 1117] the physical and technical properties of still another group of important alloys based on boron and silicon were investigated nitrides, which are mechanical mixtures of BN and Si_3N_4 and belong to the class of heterogeneous dielectrics. The specific electrical resistance of a material, containing 80% BN and 20% Si_3N_4 at 20°C is $4.5 \cdot 10^{13}$ Ω·cm, dropping at 1400° to $8 \cdot 10^4$ Ω·cm; a maximum specific electrical resistance (10^{14} Ω·cm at 20°C; $2.5 \cdot 10^5$ Ω·cm at 1400°C) is possessed by a material containing 40% BN and 60% Si_3N_4. The value of the dielectric constant has the same order, as the original components (Si_3N_4 ε - 4.4; BN - ε = = 4.25-3.2). These kinds of materials are good high-temperature insulators.

Gallium and indium nitrides are promising semiconductors of the $A^{III}B^{V}$ type [614]; the nitride alloys with other isomorphic compounds of this type are especially complex.

Transition-metal nitrides. The main properties of transition-metal nitrides, ensuring their application in technology, are their high melting points, rather good chemical stability, and also certain specific properties, such as: the ability to pass to the superconductive state, the relatively high electrical conductivity of the metallic type or the semiconductor properties. Of a certain importance are the high hardness and the wear resistance of certain nitrides. The basic area of the use of nitrides at the present time is, apparently, their application as refractory materials, possessing high melting points, a satisfactory resistance to the action of molten metals and to oxidation (especially the titanium, zirconium, tantalum, uranium and thorium nitrides [885]). Thus, in [43], the method of producing crucibles from titanium nitride was developed; in [886] - a method of manufacturing crucibles from titanium and zirconium nitrides. Alloys of MgO-TiN-Ni [197], in which TiN is a unique binder between the MgO and the nickel (TiN forms a continuous series of solid solutions with MgO and dissolves in Ni), resist thermal shocks well; their strength at 1090°C is 30% higher than at 20°C. Sometimes alloys are used in which the Ni is replaced by NiO, being reduced in the sintering process [887].

Boats, made of alloys of the Ti-B-N system are used successfully as containers for the vaporization of aluminum in vacuum metallizing. These boats are very resistant to the corroding action of molten aluminum and can be used for several days which makes it possible to organize a continuous process of metallizing steel, plastic, paper [1048].

Anti-corrosion, wear-resistant and hard coverings of nitrides are known [45], the properties of which are described in Chapter X.

As example it is possible to point to the high operational properties of spinnerets for the textile industry (the drawing of synthetic fibers), produced by the Lyon firm J. Bosyuz (France). These dies are produced by carburizing molybdenum; the surface has a hardness of 1400 H_V, and according to operational properties they are superior to steel chrome-plated spinnerets [956].

According to [1052], a good material for the manufacture of crucibles for the vaporization of aluminum is a composition of 50% TiB_2 and 50% BN, which is sufficiently electroconductive, so that it could be heated by high-frequency streams. The advantage of such heating consists in the possibility of vaporizing thin layers (films) of molten aluminum, which tends to migrate from the crucible during operation. To prevent the migration crucibles are used, the thickness of the walls of which is less than thickness of the skin-layer in the high-frequency field, which in turn depends on the specific electrical resistance of the crucible material and the frequency. Since the resistance of the composition TiB_2 + BN at 1100-1200°C (the temperature, necessary for the vaporization of aluminum) is equal to $2 \cdot 10^{-3}$ $\Omega \cdot cm$, then at frequency 200 kHz the thickness of the skin-layer is of the order of 5 mm, which also determines the selection of the thickness of the crucible wall also taking into account such factors, as the preventing of turbulence in the melt as a result of its shielding from the high-frequency field.

Titanium nitride is successfully used for dusting of the surface of casting molds for the purpose of producing of a pure casting surface.

The high hardness of certain nitrides made it possible to use them for correcting grinding wheels by burnishing with disks, for example, of cast titanium nitride [181].

Titanium and zirconium nitrides were used as the conductive material of thorium cathodes [888]; in manufacturing igniters for rectifiers a composition was used, containing 25% TiN + 75% BeO [888]. The complex titanium and chromium nitrides are recommended as high-resistance [889]. Niobium nitride is used as a detector for radio equipment, operating at 170°C [890, 891], in the construction of tubes for transmission of images [892], and also for superconductive bolometers [893, 894, 954]. In all these cases the ability of niobium nitride to change to the superconductive state is used. The addition to NbN of niobium carbide can raise the transition point to a superconductive state of up to 17-18°K [895], which makes it possible to broaden the use of the superconductive properties of niobium nitride.

Chromium nitride CrN is a promising semiconductor, in particular, for use in thermoelectric generators [327], for these same purposes scandium nitride is promising [466].

Certain nitrides, in particular chromium nitrides, are promising catalysts [899].

According to the patent [1053], transition-metal nitrides in the form of coatings on the transition metals themselves are promising materials for the manufacture of salt-ion electrodes - electrochemical instruments, intended for measuring minute acoustical pressures, the conversion of the energy of the latter into electrical energy and based on the transport of small quantities of substance in the ionic solutions [1054]. Salt-ion electrodes of transition metals (with nitride coatings) possess good electrical conductivity

and resistance to chemical and electrochemical effects, i.e., they are practically inert in a salt-ion cathode solution.

The formation of rare-earth-metal nitrides (for example, lanthanum, cerium) in steels, containing nitrogen, is one of means of improving such properties of structural steel, cold resistance and inclination to aging [934].

Uranium mononitride is a promising nuclear fuel, since in contrast to uranium carbide and dioxide it does not interact with the majority of elements, which can be used in contact with it; it has a higher thermal conductivity at temperatures greater than 800°C, than uranium monocarbide; it is less inclined toward catching fire and hydrolyzing than the carbide; it has a high uranium content, but with respect to radiation resistance it is not inferior to uranium carbide and dioxide. It can be used in fuel elements of the dispersion type, and in reactors of various types [976].

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13. ABSTRACT

The principal bases of technical progress are the development of power engineering [energetics], the automation of production and the development of new materials. Such new materials must satisfy the complex requirements of contemporary technology, possessing either individual, specific, rather clearly expressed properties, or complexes of properties. Among such materials the most promising are the refractory metals, their alloys, and also compounds of refractory metals with nonmetals - boron, carbon, nitrogen, silicon, and so forth, many of which are already being successfully used in electronics, atomic power engineering, semiconductor and dielectric technology, space technology, contemporary machine building, metallurgy, the chemical industry, electrical technology and other fields. Special interest is being manifested in compounds of metals and nonmetals and nitrogen, the so-called nitrides, among which many possess high refractoriness, dielectric and semiconductor properties, the ability to develop superconductivity at relatively high temperatures, with high chemical stability in different aggressive media, wear resistance, and others - catalytical activity, low melting points, low values of hardness, lubricating properties. [AM9024037]

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Boron Nitride						
Ionic Nitride						
Transition Metal						
Alkali Metal						
Alkaline Earth Metal						
Aluminimum						
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