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A STUDY OF EQUILIBRIUM IN A ZIRCONIUM-NITROGEN SYSTEM AT HIGH TEMPERATURES AND THE DEPENDENCE OF THE FREE ENERGY OF FORMATION OF ZrN_x ON ITS COMPOSITION AND STRUCTURE

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Ye. I. Smagina, V. S. Kutsev, and B. F. Ormont

Laboratory of Complex and Solid Compounds

The compounds of a number of metals of the transition groups with nitrogen, oxygen, and carbon, and, in particular, zirconium nitride, have enormous practical value, due primarily to their high refractoriness and thermodynamic stability. Consequently, it is important to ascertain the region of homogeneity and to find the dependence between the composition of ZrN_x, the partial pressure of nitrogen, and the temperature. The absence of appropriate data in the literature is explained by the considerable experimental difficulties involved in such investigations at high temperatures and also by the fact that a constant whole-number composition is deliberately ascribed to the above compounds, thereby excluding the possibility of studying the dependence of the properties on the composition.

The first nine references are devoted to a study of the conditions of formation of zirconium nitride and ascribe the following formulas to it: ZrN, Zr_2N_3,

Zr_2N_8, Zr_3N_2. In articles on thermodynamics written in the past few years [10,11] the formula ZrN is the one mainly used. Studies of equilibrium in nitride systems were first made by Zhukov [12], who used the tensiometric method; the reactions with Mn, Cr, Al, and other elements at temperatures up to 1570°K were studied. Attempts to carry out investigations at higher temperatures were made by Fraenkel [13], Hincke [14], Heusler [15], and Kraus [16]; however, they used ovens with carbon heaters, which resulted in the formation of carbidonitrides. The creation of a heating apparatus made of materials which are inert to the reaction components at 1500-3000°K presented great difficulties.

In a recently published paper [10] the partial pressures of decomposition of ZrN and TiN at low pressures were studied by means of the Knudsen method. The authors of this paper used the equation $ZrN = Zr + 1/2N_2$, the applicability of which was not corroborated either by chemical or by X-ray data. This error is sometimes made even in a number of reference monographs [17, 18], in which the partial pressure of nitrogen over zirconium nitride is calculated from the heat of formation according to this same equation.

Some of the thermochemical papers are high-level calorimetric studies. However, the heats of formation in these papers are either calculated [5] from the imaginary composition ZrN or are determined only for one composition [11], apparently, close to ZrN.

In studying the Zr-N system we developed a method of investigating the equilibria in the ZrN_x-N_2 system at temperatures up to 2800°K. For this purpose, we built an appropriate apparatus, which was also used for synthesizing zirconium nitrides of different compositions and for studying the conditions of

their formation. A number of nitrdies of varyable composition were obtained; they were burned in a calorimetric bomb and their heats of formation were determined [19]. The chemical equilibrium was studied in the temperature range 1900-2700°K and the pressure range 0.01-300 mm Hg. At each stage of the work the products were subjected to chemical and X-ray phase analysis.

Procedure for Equilibrium Studies

Figure 1 shows a diagram of the apparatus for investigating equilibria at high temperatures. Its principal part is vacuum oven (1) (up to 3000°K) with an electric heater made of tungsten. The oven was cooled on the outside in a thermostat (2) of 120-liter capacity, in which a temperature of 25.0°C was maintained. The oven was connected to a mercury manometer (4), a mercury seal (5), and a vacuum system joining the furnace through a trap (6) to an oil diffusion pump (12). For loading or unloading the oven, the thermostat can be raised or lowered by means of a lifting platform (3).

The initial vacuum in the oven was approximately 10^{-6} mm Hg. It was measured with a Macleod gage 16, as well as with a VIT-1 vacuum meter with thermocouple and ionization tubes. The vacuum system is connected to an oven [15] containing freshly reduced cupric oxide used for purifying the nitrogen, to a container (7) for storing the purified nitrogen, and to a Topler pump (9) for forcing the nitrogen into the oven. The temperature in the latter was measured by means of an OPPIR-45 optical pyrometer. For further accuracy a 10-ohm standard reference coil with a PP thermocouple potentiometer was connected in parallel to the galvanometer of the pyrometer in the power supply circuit. The potentiometer was calibrated in degrees Kalvin. The calibration was done by

three observers according to a standard LT-2 tube.* The three independent calibration curves were reproducible with an accuracy of $\pm 3^{\circ}$. Corrections for deviation from an absolute black body were made according to the tabular values of the blackness coefficient of tungsten. Corrections for absorption of radiation by the medium (the quartz window of the oven, the layer of water in the thermostat, and the plexiglass) were determined experimentally, by sighting the optical pyrometer alternately at the LT-2 tube through air and through the above-mentioned layer of absorbing media. The absolute accuracy of the temperature measurements was approximately 15°.

The partial pressure of nitrogen in the oven was determined from a mercury manometer: the position of the level of the mercury meniscus was determined with the aid of a cathetometer to an accuracy of 0.1 mm Hg.

We have already described the design of the oven [20]. Figure 2 shows a diagram of an improved modification of this oven. A brass vacuum cap (1) is ground into electrode (2); a vacuum lubricant serves as the seal. A molybdenum bar is screwed into an inner electrode (4), insulated from electrode (2) by a layer of picein tracing paper; a tungsten tube, heater (7), is secured to the bar by means of a collar (8). The other end of the tube is also secured by a collar and is connected to arc (5) by a series of flexible bars (9).

The temperature was measured through quartz window (3). The current from an OSU-20/6 step-down transformer was fed from a 220 v ac network to electrodes (2) and (4) via an RNO-250-10 input resonator, which was also used to control the temperature, and bars (12). In order to maintain a temperature

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*The authors take this opportunity to express their thanks to G. S. Popov for making the tube.

of 2200°K, a power of 3 kw was used (with a voltage of 3 v on a heater 12 mm in diameter).

The zirconium nitride being investigated (6) was placed on a support inside the heater. The absence of absorption of nitrogen and the results of an X-ray analysis of the solid phase attest to the fact that under the conditions of the experiment no reaction occurs between the tungsten or molybdenum heater and the nitrogen or nitride. Cf. [21-23].

In the nitridation of metallic zirconium a surface layer of nitride forms and prevents further penetration of the nitrogen by inhibiting diffusion. Compact two-phase formations are thus obtained. Therefore, in order to study the equilibrium, we used as starting material previously nitrided zirconium, zirconium nitride in powder form. The metallic zirconium contained 99.7% metal, including hafnium; according to spectral data* the latter was present to the extent of ~1%. Zirconium contained the following percentages of other impurities: Fe - 0.03, Ca - 0.04, and Cl - 0.002%. In studying the equilibrium, 3 g of zirconium nitride were loaded into the previously ignited heater. By gradually heating the system up to 1500°K and raising the vacuum, the gases were desorbed from the nitrides and the parts of the apparatus. Then the equilibrium pressure was determined by the static method. For this purpose, the oven was filled with nitrogen at a constant temperature at pressures up to ~ 0.5-1 atm. The initial zirconium nitride, ranging in composition from $ZrN_{0.6}$ to $ZrN_{0.8}$, absorbed nitrogen, the pressure fell, and after approximately 30 min, remained constant.

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*The authors wish to thank S. M. Solodovnik (Giredmet) for analyzing the hafnium concentration.

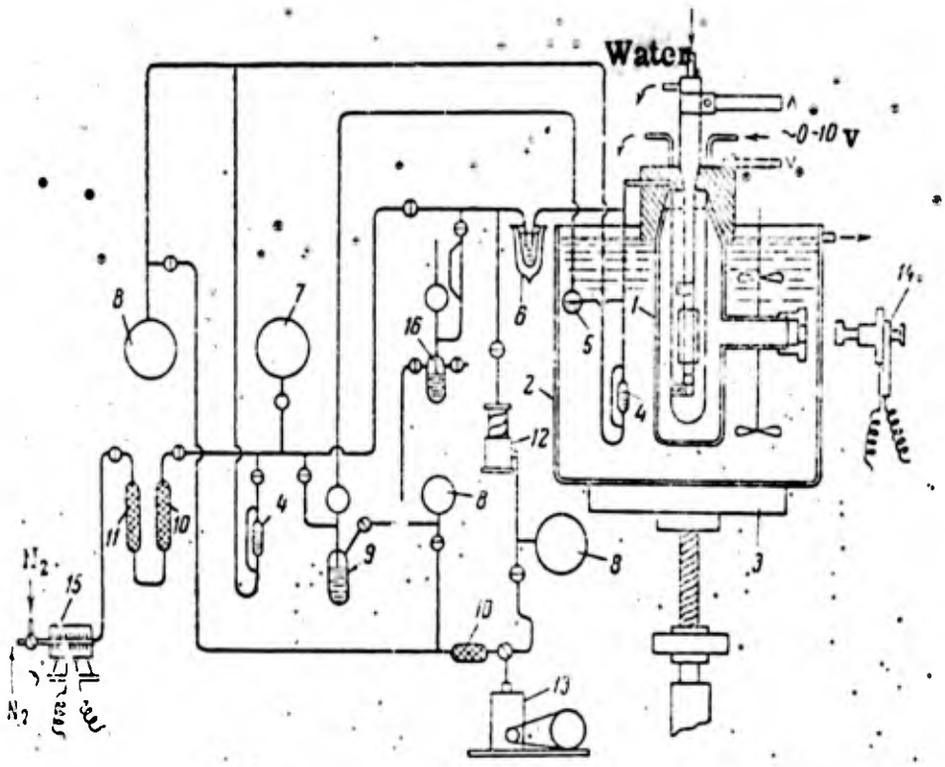

Fig. 1. Diagram of the apparatus for investigating equilibria: 1) vacuum oven; 2) thermostat; 3) lifting platform; 4) mercury manometers; 5) mercury seal; 6) trap containing liquid nitrogen; 7) reserve flask for N_2; 8) reserve flasks; 9) topler pump; 10) tube containing P_2O_5; 11) tube containing NaOH; 12) diffusion pump; 13) low vacuum pump; 14) optical pyrometer; 15) Mars oven; 16) Macleod gage.

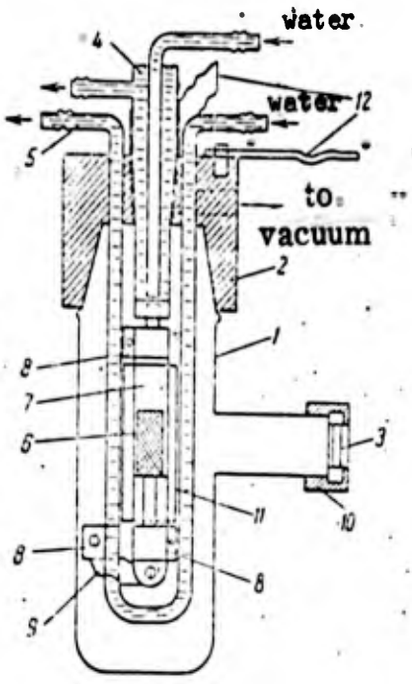

Fig. 2. Diagram of vacuum oven. 1) vacuum cap; 2) electrode; 3) quartz window; 4) inner electrode; 5) copper arc; 6) nitride being investigated; 7) tungsten heater; 8) molybdenum collars; 9) series of molybdenum bars; 10) sleeve nut; 11) molybdenum shield; 12) current-feeding bars.

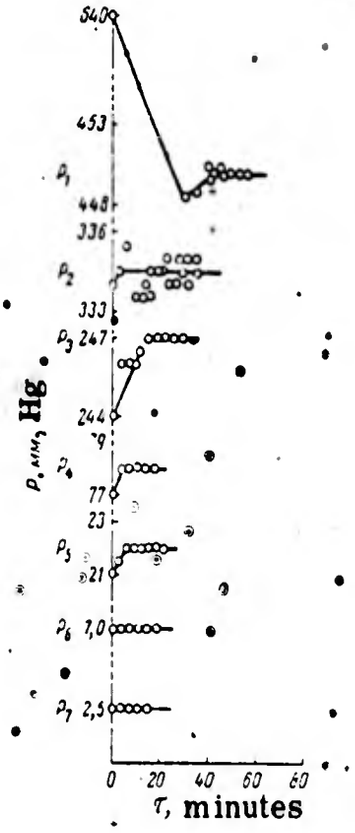

Fig. 3. Example of the determination of equilibrium pressures by the static method T = 2350°K.

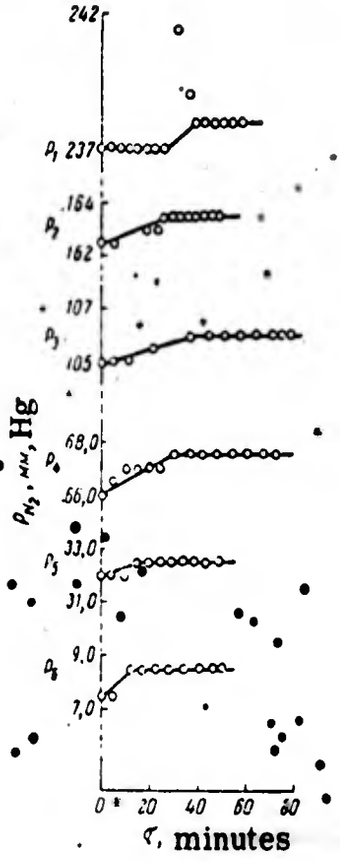

Fig. 4. Example of the determination of equilibrium pressures when T = 2320°K.

In order to study the dependence of the composition of ZrN_x on the pressure at a given temperature, preparations at nitrogen pressures ranging from 0.01 to 200 mm Hg were exposed until a constant pressure was reached (cf. Figs. 3 and 4); the pressures were varied either by injecting gas through a Topler pump or by evacuating the system with a vacuum pump.

In order to ascertain whether the true equilibrium had been reached, control experiments were run. When the pressure was increased up to P_1 (approximately 15 mm above the equilibrium pressure), a decrease in the pressure, due to absorption of nitrogen, was observed. When the pressure was decreased down to P_2 (approximately 15 mm below the equilibrium pressure), an increase in the pressure was observed (cf. Fig. 5). As is known from the literature, the rate of the reaction (at a given temperature) depends on how much the pressure of the gas phase differs from the differs from the equilibrium pressure. The greater this difference, the greater the rate of absorption or liberation of nitrogen from the nitride phase. This pattern is observed to some extent when studying single variant equilibria in oxycarbide phases [24], thus making it possible for us to find the equilibrium pressures in the dynamic method by extrapolating the curves $v = f(P)$ to $v = O$.

In our case of multiple variant equilibrium this pattern is not observed. This is due apparently to a more complex type of equilibrium, a poor rate of diffusion, and recrystallization processes. Therefore we did not extrapolate to $v = \frac{\Delta P}{\Delta \tau} = 0$, and in checking the veritability of the equilibrium, we judged, not by the magnitude of the rate $\frac{\Delta P}{\Delta \tau}$, but only by its sign. The pressure rises or falls, when the state of equilibrium deviates in one or the other direction.

The literature contains descriptions of methods of determining equilibrium. These methods were used in studies of oxycarbide systems [24-26]. We used a method for determining equilibrium used previously [25, 26] for studying the system TiC_xO_y-C-CO. Figure 3 shows the determination of equilibrium compositions and pressures, when the composition of the initial nitride was far from equilibrium; in Fig. 4 the composition of the initial nitride was close to equilibrium. For each temperature the chemical and phase composition of the initial and final products was determined. However, the accuracy of the chemical analysis in certain cases was inadequate for determining the changes in the composition of the nitride, since these changes were not always great. Moreover, it was desirable to have the characteristic of the intermediate compositions at one temperature and different pressures. Therefore the volume of the apparatus was calibrated at a constant temperature (25°C). This enabled us to determine the relative change in the composition of the nitride from the increase or decrease in the pressure of the nitrogen in the system by calculating from the original composition of the initial nitride (or final composition) determined by chemical analysis.

Methods of Thermochemical Investigation[19]

Zirconium nitrides of compositions ranging from $ZrN_{0.56}$ to $ZrN_{1.0}$ were subjected to calorimetric combustion. The majority of samples were obtained under equilibrium conditions. A portion of the nitrides contained traces of oxygen.

The combustion was carried out in a calorimetric bomb of the Berthelot-Crocker type of reduced dimensions. The temperature of the water in the

isothermal jacket was determined before each experiment in relation to the room temperature. The heat value of the calorimeter was determined from standard benzoic acid samples obtained at the D. I. Mendeleyev Metrological Institute in Leningrad with a heat of combustion of 6329 cal/g. From seven determinations the heat value of the calorimeter was found to be 992.3 kal/g. The most complete combustion conditions were established beforehand. The best results were obtained when the nitrides were burned in the form of powder freely applied on cotton fabric. The compound sample was ignited with the aid of a platinum wire 0.01 mm in diameter, melted by a current from a step-down transformer. The wire was joined by a cotton thread to the fabric on which approximately 600 mg of nitride were to be burned. In order to avoid a reaction between the nitride and the quartz at the combustion temperature, which reached approximately 2000°C, the nitride was placed in a quartz crucible with a lining made of previously ignited zirconium oxide*. The best combustion took place at an oxygen pressure of 16 atm. At higher pressures the combustion products were sparyed over the bomb, thus making it more difficult to determine the degree of completeness of combustion. The initial and final combustion periods amounted to 10 min, while the main period was 8 - 10 min. The temperature increase amounted to approximately 1.2° and was measured with a Beckmann thermometer. The observed temperature increase was corrected for heat losses from the calorimeter to the external medium, the temperature of the protruding column, and the heat generated by the current passing through the platinum filament; the latter correction was estimated from the voltage, the amperage,

*Ignition was essential, since zirconium dioxide is capable of adsorbing up to 0.5% moisture.

and the time.

The correction for the incomplete combustion of the nitride and the primer is essential. It should be noted that this correction basically determines the accuracy of the experiment and overlaps the inaccuracy in measuring the temperature, an inaccuracy which, in principle, could be reduced by using semiconductor thermistors [27].

In order to introduce the corrections for incomplete combustion, the products were subjected to X-ray and chemical analyses. The quantity of unburned nitride and carbon was determined by igniting the quartz crubible containing the products after calorimetric combustion in an oxygen current at 1200°C. The quantity of unburned nitride was calculated from the gain in weight of the crucible, while the quantity of unburned carbon was calculated from the gain in weight of the "boat" containing the alkali. According to the X-ray analysis the nitride burns to zirconium dioxide of monoclinic syngony.

Table 1 gives an example of the heat balance with all the corrections taken into account.

The X-ray and Chemical Analysis

The phase composition of the nitrides was controlled by X-ray methods. The powder applied on a glass capillary was photographed on collodion with a camera 86 mm in diameter, by Cu_{k_α} -radiation with an asymmetric arrangement of the film. In addition, the samples were photographed on URS-50 I. The specimens were applied by means of tsapon-lak (a cellulose-nitrate varnish) to a cardboard pressboard in the form of a circle 10 mm in diameter and with a specimen layer approximately 0.5 mm thick. The photographing was done at

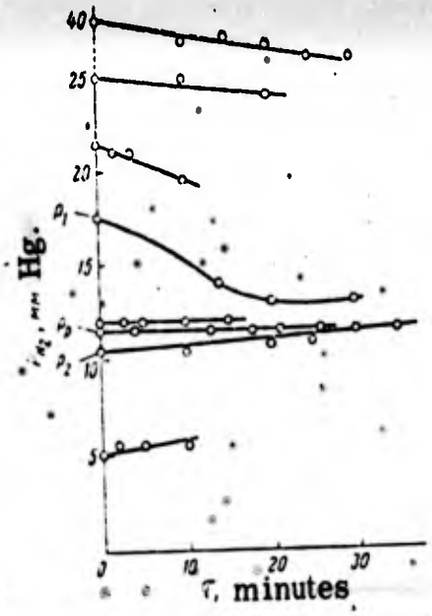

Fig. 5. Control experiment for checking whether equilibrium has been reached at $P_0 \approx 12$; $P_1 = 17.5$; 21.5; 25; 40 and $P_2 = 10.5$ and 5.0 mm Hg.

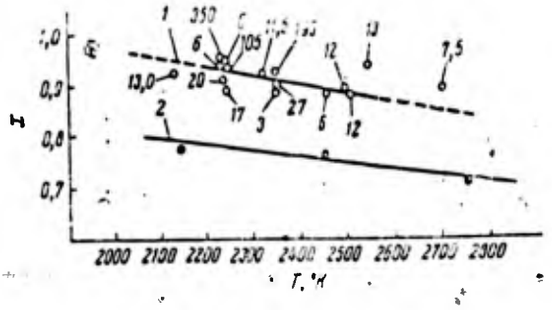

Fig. 6. The dependence of the composition of ZrN_x on temperature: 1. for P ≈ 10 to 100 mm Hg; 2. for P ≈ 10^{-1} mm Hg.

the rate of 2° per minute. All the preparations were single-phase nitrides with a face-centered cubic cell and a lattice period varying (according to the most accurate data) from 4.583 to 4.577 A.

The method of analyzing zirconium nitride is not described in the literature. Individual articles [2, 9, 28-30] contain only instructions to use the Dumas or the Kjeldahl method when analyzing such compounds for nitrogen. We preferred the Kjeldahl method.

In order to carry out the analysis, we used concentrated sulfuric acid, which completely dissolves zirconium nitride on heating (in contrast to the nitride, metallic zirconium does not dissolve in sulfuric acid).

The analyses were made by the semimicro method. Small weighed portions of the nitride ($\sim$170 mg) and 40-50 cm^3 of sulfuric acid were used for the analysis. After cooling, the solution was poured into a volumetric flask; 25 cm^3 aliquots were taken and decomposed in a Kjeldahl flask with a concentrated solution of alkali. The flask connected by a ground joint to a Liebig condenser and to a separatory funnel containing the alkali; the tip of the condenser was lowered into the flask containing a titrimetric solution of sulfuric acid. The ammonia vapor given off during the decomposition of ammonium sulfate was absorbed by the water vapor in the Liebig condenser; the solution thus obtained flowed into titrimetric sulfuric acid. The quantity of ammonia was determined by back titration with alkali.

The amount of zirconium in the nitride was determined by burning a weighed portion ($\sim$.200 mg) in a muffle furnace at $1000^{\circ}C$ for 2 hours and then weighing the zirconium dioxide which is formed.

The accuracy of the determinations for nitrogen and zirconium was 0.1%.

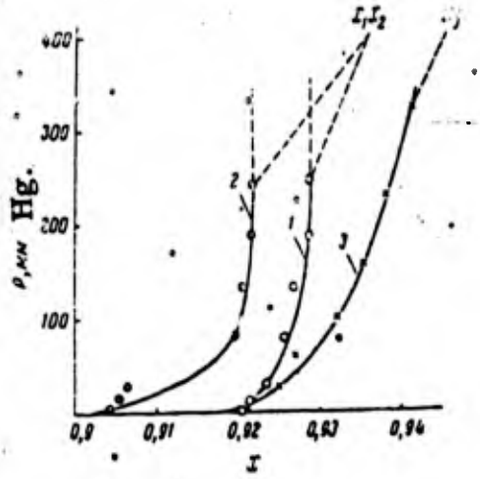

Fig. 7. The dependence of the composition of ZrN_x on pressure (according to tensivolumetric data):

1-2 - when T = 2235°K; 3 - when T = 2320°K

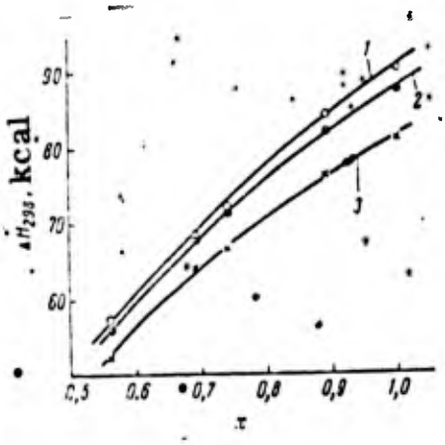

Fig. 8. The dependence of ΔH^o and ΔF^o on the composition of the nitride:
1. for ZrN_xO_y - $\Delta H^o_{298} = f_1(x)$; 2. for ZrN_x - $\Delta H^o_{298} = f_2(x)$; 3. for ZrN_x - $\Delta F^o_{298} = f_3(x)$.

TABLE 1

Heat and Mass Balance of Calorimetric Combustions

Combustion product	molecular weight	combustion number	weighed portion of ZrN_x, g	Heat generated cal. Total	from primer	from the combustion of the nitride	heat of combustion of ZrN_x, cal/g	weight of unburned carbon, mg	correction for heat of unburned carbon cal.	weight of unburned ZrN_x, g	weight of burned ZrN_x, g	Weight of combustion of ZrN_x after introduction of the correction kcal/g	kcal/mole	Q_v of formation, kcal/mole	Q_p of formation, kcal/mole	Q_p of formation, kcal/mole
$Zr_1N_{0.563}O_{0.02}$	109.2	1	0,6009	1367,81	167,87	1199,94	1996,9	2,5	19,5	0,0062	0,5947	2050,5	205,16	201,03 ± 0,7	57,2 ± 0,7	57,5 ± 0,7
		2	0,6066	1385,77	167,47	1218,30	2008,1	1,34	10,45	0,0018	0,6048	2031,6	203,56			
		3	0,6011	1387,26	177,51	1209,75	2012,5	1,4	10,92	0,0021	0,5990	2037,8	201,19			
$Zr_1N_{0.89}O_{0.03}$	105,50	1	0,6085	1161,71	181,92	979,79	1610,2	2,7	21,06	0,0141	0,5944	1683,7	177,6	177,27 ± 0,45	84,23 ± 0,45	81,5 ± 0,45
		2	0,6071	1151,19	192,23	958,96	1579,5	3,8	29,64	0,0198	0,5873	1683,3	177,58			
		3	0,6109	1142,06	150,32	991,74	1623,3	2,3	17,91	0,0079	0,6030	1674,4	176,65			

TABLE 2

The Dependence of the Composition of Zirconium Nitrides on Temperature and Pressure

Formula of the initial product	True temperature of the furnace °K	P_{N_2}, mm Hg	Chemical analysis of the final product: N, %		Zr, %		Formula	Lattice period
Nitride with low nitrogen content	2133	13,0	12,51 12,13 12,08	12,24	87,23 87,38 87,53	87,38	$Zr_1 N_{0,924} O_{0,02}$	$4,577_3$
$Zr_1 N_{0,937}$	2148	0,15	10,53 10,2	10,35	88,3 88,35 88,2	88,3	$Zr_1 N_{0,783} O_{0,08}$	$4,578_3$
$Zr_1N_{0,935} O_{0,01}$	2235	2,0	12,43 12,43 12,38 12,32 12,52 12,59	12,5	87,49 87,50	87,5	$Zr_1 N_{0,941}$	$4,576_9$
$Zr_1 N_{0,935} O_{0,01}$	2235	6,0	12,72 12,66 12,55	12,63	87,7 87,6	87,6	$Zr_1 N_{0,948}$	$4,577_6$
$Zr_1 N_{0,658}$	2235	17,0	12,37 12,28 12,23	12,3	87,7 87,65	87,67	$Zr_1 N_{0,89}$	$4,577_0$
$Zr_1 N_{0,804}$	2235	20,0	12,3 12,1	12,2	87,6 87,5	87,55	$Zr_1 N_{0,92}$	$4,577_5$
$Zr_1 N_{0,967}$	2235	109,0		12,63	87,8 87,8 87,8	87,8	$Zr_1 N_{0,905}$	$4,577_1$
Nitride with low nitrogen content	2235	350,0	12,70 12,74	12,01	87,92 87,90	87,91	$Zr_1 N_{0,952}$	$4,577_1$
$Zr_1 N_{0,956}$	2320	11,5	12,53 12,57 12,53	12,54	87,7 87,9	87,8	$Zr_1 N_{0,941}$	$4,578_3$
$Zr_1 N_{0,731}$	2350	3,0	11,33 11,37 11,41	11,37	86,83 86,45 87,0	86,91	$Zr_1 N_{0,67}$	$4,577_0$
$Zr_1 N_{0,935} O_{0,01}$	2350	27,5	11,91 11,98 11,90	11,93	88,1 88,1	88,1	$Zr_1 N_{0,895}$	$4,578_7$

TABLE 2 - continued

: The Dependence of the Composition of Zirconium Nitrides on Temperature and Pressures

Formula of the initial product	True temperature of the furnace T_K	P_p, mm Hg.	Chemical analysis of the final product: N, %		Zr, %		Formula	Lattice period
Nitride with nitrogen content	2353	195,0	12,13 12,1 12,67 12,58	12,37	88,09 87,81 88,04	87,98	$Zr_1 N_{0,928}$	4,575
$Zr_1 N_{0,783}$	2448	0,23	10,50 10,02	10,26	88,0 88,2 88,1	88,1	$Zr_1 N_{0,765} O_{0,1}$	4,582
$Zr_1 N_{0,956}$	2455	6,0	11,81 11,78 11,84	11,81	88,2 88,4	88,3	$Zr_1 N_{0,883}$	4,576
Nitride with nitrogen content	2505	12,0	11,82 11,80	11,81	87,86 87,61	87,73	$Zr_1 N_{0,855} O_{0,03}$	4,577
Nitride with nitrogen content	2505	12,0	11,83 11,69	11,77	87,80 87,93	87,86	$Zr_1 N_{0,852}$	4,577
$Zr_1 N_{0,898} O_{0,01}$	2545	13,0	12,42 12,45 12,48	12,45	87,83 87,97	87,9	$Zr_1 N_{0,931}$	4,576
$Zr_1 N_{0,935} O_{0,01}$	2700	7,5	11,96 11,94 11,98	11,96	87,9 87,8	87,85	$Zr_1 N_{0,894}$	4,577
$Zr_1 N_{0,935} O_{0,01}$	2750	0,01	8,78 8,85 9,2	8,94	92,9 92,9	92,9	$Zr_1 N_{0,70} O_{0,02}$	4,583
Zirconium powder	2630	Pressure not stabilized	3,27 13,29	13,28		86,14	$Zr_1 N_1 O_{0,04}$	4,577
$Zr_1 N_{0,683} + Zr$	2320	Pressure not stabilized	7,76 7,88 7,93	7,86	91,55 91,52 92,29 92,05	91,43	$Zr_1 N_{0,563}$	4,583

TABLE 3.

The Dependence of the Composition of Zirconium on Temperature and Pressure

Initial composition of zirconium nitride	Weighed portion, g	T, °K	Equilibrium pressure, mm Hg	Holding hours	Composition of zirconium nitride (according to chemical analysis
$Zr_1 N_{0.935} O_{0.01}$	1.39	2660	$4 \cdot 10^{-3}$	13	$Zr_1 N_{0.708} O_{0.02}$
$Zr_1 N_{0.935} O_{0.01}$	2.0	2750	$5 \cdot 10^{-3}$	8	$Zr_1 N_{0.70}$
$Zr_1 N_{0.935} O_{0.01}$	2.0	2820	$3.5 \cdot 10^{-3}$	10	$Zr_1 N_{0.768}$

TABLE

TABLE 4

The Dependence of Equilibrium Compositions on Pressure (when T = Const.)

Test temperature, $^{\circ}K$	Initial composition of zirconium nitride	Pressure, mm Hg			Length of test, minutes	Equilibrium composition of zirconium nitride
		P_{init}	P	P_{equal}		
2235	$ZrN_{0.935}$	254	3,0	251,0	160	$ZrN_{0.929}$
	$ZrN_{0.929}$	192	0	192,0	50	$ZrN_{0.929}$
	$ZrN_{0.929}$	140	1,0	139,0	90	$ZrN_{0.927}$
	$ZrN_{0.927}$	84	0,5	83,5	50	$ZrN_{0.926}$
	$ZrN_{0.926}$	36	1,0	35,0	85	$ZrN_{0.924}$
	$ZrN_{0.924}$	19	1,0	18,0	60	$ZrN_{0.922}$
	$ZrN_{0.922}$	6,0	0,5	5,5	43	$ZrN_{0.921}$
2235	$ZrN_{0.945}$	250	5	245	180	$ZrN_{0.922}$
	$ZrN_{0.922}$	194	0	194	25	$ZrN_{0.922}$
	$ZrN_{0.922}$	140	0,5	139,5	90	$ZrN_{0.921}$
	$ZrN_{0.921}$	84	0,5	83,5	45	$ZrN_{0.920}$
	$ZrN_{0.920}$	35	5,0	30	120	$ZrN_{0.907}$
	$ZrN_{0.907}$	18	0,5	17,5	80	$ZrN_{0.906}$
	$ZrN_{0.906}$	6,0	0,5	5,5	75	$ZrN_{0.905}$
2320	$ZrN_{0.946}$	331	1,5	329,5	110	$ZrN_{0.941}$
	$ZrN_{0.941}$	238	1,0	237	48	$ZrN_{0.938}$
	$ZrN_{0.938}$	163,5	1,0	162,5	110	$ZrN_{0.935}$
	$ZrN_{0.935}$	106	1,0	105	85	$ZrN_{0.932}$
	$ZrN_{0.932}$	67	1,5	65,5	75	$ZrN_{0.927}$
	$ZrN_{0.927}$	32	0,5	31,5	60	$ZrN_{0.925}$
	$ZrN_{0.925}$	11,5	1,5	10,0	50	$ZrN_{0.921}$

TABLE 5

The Dependence of the Heats and Free Energies of Formation of Zirconium Nitrides on Compositions

Nitride	Q_p, kcal/mole	Q, kcal/mole	ΔS^0_{298}	S^0_{298} ZrN_x	ΔF^0_{298}
ZrN_1 $O_{0,04}$	90,7 ± 0,2	87,9	—22,9	9,3	—81,1
$ZrN_{0,89}$ $O_{0,03}$	84,5 ± 0,5	82,4	—20,4	9,25	—76,3
$ZrN_{0,74}$ $O_{0,00}$	72,2 ± 0,9	72,2	—16,5	9,7	—67,3
$ZrN_{0,69}$ $O_{0,00}$	68,7 ± 1,8	68,7	—15,4	9,7	—64,1
$ZrN_{0,56}$ $O_{0,02}$	57,5 ± 0,7	56,1	—12,7	9,4	—52,3

The oxygen content in the nitride was determined from the difference.

The results of the study attest to the fact that the nitride phase ZrN_x exists in equilibrium with nitrogen; the metallic phase of zirconium is absent in this case. Tables 2 and 3 contain data concerning the dependence of the equilibrium compositions on pressure and temperature. The lattic periods of the respective nitrides are also given.

In the temperature range 2100-2750°K and the pressure range 10-100 mm Hg the nitride compositions depend mainly on temperature and only slightly on pressure, as can be seen from the graph given in Fig. 6, where the points corresponding to these pressures are approximated by a straightlline. In the interval 0.1-10 mm Hg the composition already depends essentially on the pressure (Fig. 7); the change in composition in this case was calculated from the quantity of absorbed or liberated nitrogen, proportional to the change in pressure (Table 4). As was mentioned above, the accuracy of the chemical analysis did not enable us to ascertain this dependence. The readings were made from the initial compositions $x_1 = x_2 = 0.935$ and $x_3 = 0.956$ established by chemical analysis with an accuracy not exceeding ± 0.01. This circumstance explains the mutual shift of curves 1 and 2 (cf. Fig. 7) when T = 2235°K along the y-axis by the magnitude $\Delta x = 0.004$ and also explaind the shift of curve 3 into the region of compounds richer in nitrogen. This graph also shows clearly the great stability of the composition of the nitrides in the range of higher pressures. In the range 100-300 mm Hg the change in composition does not exceed thousandth parts of the magnitude of x. Extrapolation of the compositions to higher pressures is possible.

As can be seen from Table 2, when identical P and T are established,

regardless of the compositions of the initial nitrides, the equilibirum compositions are identical within the limits $\Delta x = 0.015$, which once again corroborates the verity of the equilibria attained.

From the phase and chemical composition of the system being studied (absence of Zr) it follows that the decomposition of zirconium nitride does not proceed according to the equation given in the literature

$$ZrN = Zr + \frac{1}{2} N_2$$

Given a gradual change in pressure and temperature, the change in the composition of the nitride ZrN_x proceeds according to the equation

$$ZrN_x = ZrN_{x-\Delta} + \frac{\Delta}{2} N_2$$

In this case, when the temperature increases or the pressure decreases, the value of x decreases. Thus the composition $ZrN_{1.0}$ must be regarded as a rarely realized case. From the data of the thermochemical study (Table 5) according to the equation

$$ZrN_xO_y + \left(1 - \frac{y}{2}\right) O_2 = ZrO_2 + \frac{x}{2} N_2$$

the heats of formation Q_p of the nitrides ZrN_x were calculated. The oxygen and hafnium (1%) content was taken into account in the calculation. For more details see [19]. The data for the enthalpy of oxygen-free nitrides in relation to the composition are shown in Fig. 8. Using the gain in entropy of nitrogen and zirconium in a number of homologs [19, 31], we calculated the values of the entropy of ZrN_x and plotted a curve showing the dependence of the free enthalpy of formation on the value of x. In the calculation the configuration parts of the entropy were taken into account according to the equation

$$S^k = R[x \ln x + (1 - x) \ln (1-x)]$$

where x is the portion of the points of the unit nitride cell occupied by nitrogen; (1 - x) is the portion of the lattice points not occupied by nitrogen.

A Study of the Conditions of Formation of Nitrides of Given Compositions

The procedure developed and the equilibrium data obtained with its aid enable us to ascertain the optimal conditions for synthesizing zirconium nitrides of given composition, conditions which can be recommended for large scale operation.

The nitrides are synthesized in two stages.

Stage 1. A larger heater, 30 mm in diameter and 80 mm long, made of molybdenum sheeting is introduced into an overn of the above-described design. The heater is loaded with approximately 50 g of zirconium powder moistened with water*. In order to facilitate the diffusion processes during the nitridation the powder should not be loaded in layers that are too dense. Then the moisture and sorbed gases are evacuated. The moisture is absorbed in a tube containing phosphoric anhydride. As the vacuum is increased (up to 10^{-3} mm Hg), the

*We must mention the danger of working with dry zirconium, which is pyrophoric and readily explodes when rubbed.

temperature of the furnace is raised up to 1100-1200°K. After reaching this temperature the furnace is filled with nitrogen, which is quickly absorbed. After 30 minutes, when the process slows down, the temperature is increased to 1500-1600°K, and the nitridation continued for another 3-4 hours, until no more nitrogen is absorbed.

The product unloaded from the oven has the form of a not compactly sintered mass, which readily crumbles into powder in a porcelain mortar. As a rule, the sample consists of two phases, the nitride and the unreacted zirconium residue; it contains 9-10% nitrogen.

Stage 2. The sample obtained is loaded into a tungsten beaker and is subjected again to nitridation in a tungsten heater. As in the first stage, the gases are first desorbed by heating up to 1500°K. Then the nitrogen is fed in, and the temperature is increased to the value corresponding to the required nitride composition. In this case we use the data given in Tables 2 and 3 concerning the dependence of the equilibrium composition of the zirconium nitrides on temperature and pressure. The nitridation is continued until a constant pressure is reached; this takes about 2 hours.

Thus nitrides of compositions ranging from $ZrN_{0.85}$ to $ZrN_{0.95}$ should be obtained at temperatures from 2100 to 2750°K and nitrogen pressures of 10-100 mm Hg. Nitrides of compositions ranging from $ZrN_{0.7}$ to $ZrN_{0.8}$ are obtained at these same temperatures but at pressures of the order of 0.1 mm Hg. Poorer and single-phase nitrides (of composition up to $ZrN_{0.6}$) could only be obtained by sintering the appropriate mixtures of nitrides and zirconium at 2000-2300°K. The composition $Zr_{1.0}N_{1.0}O_{0.04}$ could not be reproduced. Probably a higher pressure and more time are required for its synthesis. As

the stoichiometric composition $ZrN_{1.0}$ is approached, the color of the nitride changes from grayish-yellow to greenish. The preparation was ground in steel Abegg mortars, after which the iron was washed off with dilute hydrochloric acid.

Conclusions

1. A method of studying equilibria in refractory nitride systems at 1500-2800°K was developed.

2. The equilibrium in the system ZrN_x - N_2 was studied in the temperature range 2000-2800°K, the pressure range 0.1-300 mm Hg, and a range of change in x from 0.7 to 1.0. The dependence of the equilibrium compositions on temperature and pressure was established. The composition ZrN is a special case. The decomposition equation equation used in the literature

$$ZrN = Zr + \frac{1}{2}N_2$$

was not corroborated at the pressures and temperatures investigated by us.

3. As the composition of ZrN_x changes, the heats and free energies of formation change considerably; this must be taken into account in thermodynamic calculations. As the composition changes from $ZrN_{0.56}$ to $ZrN_{1.0}$, the heats of formation change from 56,100 to 87,900 cal/mole.

4. The conditions of formation of zirconium nitrides of given composition were studied, and a method of synthesizing them was developed.

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