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by

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The purpose of the present investigation is to plot the boundaries of the phase zones of the ternary system chromium-nickel-niobium limiting ourselves to that portion of the concentration triangle between a line for the binary chromium-nickel alloys and a line connecting intermetallic compounds $NbCr_2$ and Ni_3Nb (Fig.1).

Fig.1 - Isothermic Section through Phase Diagram of Ternary Chromium-Nickel-Niobium System at 1100°

The literature contains data with respect to attempts to produce heat-resistant alloys within the chromium-nickel-niobium ternary system by the addition of a fourth element (Bibl.1), but no studies exist with respect to the investigation of the phase diagram of this ternary system. Only in (Bibl.2) was a report presented on the melting of a number of alloys with compositions lying within the triangle along a line connecting the nickel and intermetallic compound $NbCr_2$. However, no conclusions with respect to the character of this diagram was drawn.

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The binary systems constituting the side of a triangle have been investigated to a greater or lesser degree in works by various authors. The Ni-Nb system has been investigated in a number of works (Bibl.3,4). The Study (Bibl.4) is the most reliable, and is in accordance with its data; the portion of the phase diagram of this system that is of interest to us is presented in Fig.1. It constitutes a diagram with an eutectic transformation at 1270°. The maximum solubility of niobium in nickel at the eutectic temperature is observed at 20 wt.%. The second phase entering into the composition of the eutectic is an intermetallic compound Ni_3Nb the melting point of which is 1400°.

The chromium-niobium system was investigated in (Bibl.2,5-9). As indicated in Fig.1, a eutectic transformation exists at 1625° (Bibl.9) in this system in the interval of concentrations of interest to us. The eutectic is formed by a solid solution of niobium in chromium (approximately 15% Nb) and the intermetallic compound $NbCr_2$. The latter has a melting point in the vicinity of 1700°.

The greatest number of investigations has been in the chromium-nickel system. However, there are significant difference both with respect to the alloys enriched in nickel and with respect to the specific features of the chromium side of the diagram in terms of the form of the phase change diagram of this system.

Chromium-Nickel Binary System

Starting with Matsunaga (Bibl.10), all investigators held, until recently, that the constitution diagram of a chromium-nickel system was one of the simplest eutectic type with limited solubility of the components. According to the data of (Bibl.11-13), the eutectic temperature is 1343°, the eutectic point is at 49 wt.% of Ni, and the maximum concentration at the temperature of eutectic transformation of the chromium-base solid solution is 40.5 wt.% Ni whereas that of the nickel-base solid solution is 54 wt.% Ni. However, inasmuch as the hypothesis that a polymorphic transformation

existed in chromium at 1840°, was made in (Bibl.14-17), whereas a eutectoid transformation existed at 1215° in the chromium-nickel system, the opinions of the investigators were in agreement.

An investigation of a binary system consisting of chromium and tantalum was presented in the report of A.T.Grigor'yev, A.N.Gusev, Ye.A.Sokolovskoya, L.A.Panteleymonov, and V.V.Kuprina at the 1958 Conference on Heat-Resistant Alloys. The presence of a polymorphic transformation in chromium at 1815° and of a eutectoid transformation at 1450° was demonstrated.

It should be noted that in (Bibl.15,17), a face-centered cubic crystal lattice with 3.68 Å as parameter is being ascribed to the high-temperature chromium phase (Bibl.17). However, the paper by A.T.Trigor'yev and others shows this phase to have a body-centered cubic lattice, i.e., the same as at low temperature. The hypothesis is offered that chromium may contain two polymorphic transformations as is the case in iron, $\alpha \rightarrow \gamma$ and $\gamma \rightarrow \delta$, the phases α and δ being isomorphic. In (Bibl.18), the β-phase of chromium, which forms upon addition of tenths and hundredths of a percent of boron to chromium at a temperature of ~1300° is hypothesized to have an hexagonal lattice (a = 2.5710 ± 8 KX, c = 4.4399 ± 6 KX, c/a = 1.614).

242 In our view, all the data in favor of the existence of a transformation in chromium and a eutectoid transformation in the chromium-nickel system are dubious to a greater or lesser degree, in the sense that they are either subject to other-than-unique interpretations, or that the purity of experimentation was not exceptionally high when they were derived.

It is shown in a work by Williams (Bibl.13) that the decomposition of a solid solution, which is taken by some authors to be a eutectoid as a consequence of aging, is related to rapid reduction in the solubility of nickel in chromium with reduction in

temperature (at temperatures of less than 700 - 800°, nickel is virtually insoluble in chromium). Considerable divergence is found in the determinations of the solubility curve by various investigators (Bibl.11, 12,13,15,16).

The purpose of the present study was to provide confirmation for basis for refuting the existence of a eutectoid reaction in the chromium-nickel system as well as to verify the solubility data.

The following were the initial materials for the preparation of the alloys: electrolytic chromium refined by annealing and hydrogen, and containin the following impurities: 0.0022% O, 0.009% N, 0.04% Si, and electrolytic nickel, grade 0000. The bulk of the alloys were melted in an arc furnace with tungsten electrode and water-cooled copper molds, in an argon atmosphere purified by the melting of a getter of metallic titanium. The ingots, weighing 40 gm, were remelted as many as 6 times, with rotation. Eight alloys were made in this manner. Chip was taken from the top and bottom of each ingot for chemical control analysis. The differences in the chemical analysis of the upper and lower portions proved to be insignificant. The chemical analysis indicated the following impurities to be present in the alloys (including the ternary alloys): 0.004% W, 0.066% Cu, 0.003% Si. Pieces were cut from the ingot for investigation in the initial condition, while the rest was annealed at 1100° for 107 hrs in an atmosphere of purified argon, and then gradually cooled with the furnace. Samples were cut from the annealed specimens for microstructural hardness, and dilatometric studies (these specimens were 50 mm long and 4 mm in diameter), as well x-ray
Specimens for Debye and back-reflection crystal analysis.

Some additional alloys were made in Tammann furnace and in aluminum oxide crucibles, in which cases the nickel was melted first, whereupon pressed chromium briquets were added to a molten melt. Rods were made from the alloys by sucking into quartz tubes.

242 The carbon content of the alloys did not exceed 0.02 - 0.03%. These alloys were also subjected to annealing at 1150° for 50 hrs in an atmosphere of purified argon and were cooled slowly together with the furnace. Specimens were then made from them for dilatometric, microscopic, and x-ray crystal analysis.

Table 1 presents the compositions of all the chromium-nickel binary alloys melted.

The dilatometric specimens of virtually all the alloys were investigated in the annealed condition on a high-sensitivity vertical dilatometer, in which the use of a special optical-mechanical device made it possible to magnify by about 6000 times, and the use of aluminum oxide tubes and pushers made it possible to heat to 1350°. The dilatometric curves of all specimens were taken in the interval from room temperature to onset of fusion. Figure 2 presents specimens of the curves obtained. Virtually all the curves are completely mutually identical, and consist of two nearly rectilinear

243 sections, connected by a smooth rounding-off. At low temperatures, the coefficient of

Table 1

Arc furnace	Tammann furnace
" "	" "
" "	" "
Tammann furnace	Arc furnace
Arc furnace	Tammann furnace
" "	Arc furnace
Tammann furnace	" "
" "	Tammann furnace

a) Nickel content, wt.%; b) Method of melting

linear expansion is about one half that at high temperature. The highest rate of change in the coefficient of linear expansion in the curves is found in the 850 - 900° range. On the dilatogram of an alloy containing 22.02% Ni at 1150° there is yet another point at which the coefficient of linear expansion varies (in the direction of reduction). The lower point inflection apparently relates to the onset of solution of the γ-phase

in the γ-phase of Cr, and the upper point relates to the transition through the solubility curve or, in other words, to termination of the solution of the γ-phase. No other anomalies of the dilatogram were observed, clear up to the solidus.

A specimen of the annealed alloy containing 32.6% Ni was subjected to differential

Fig.2 -- Example of a Dilatogram, Taken on a High-Sensitivity Vertical Dilatometer, for Chromium - Nickel Alloys of in the Annealed State:

1 - 22.02% Ni; 2 - 32.6% Ni; 3 - 35.8% Ni

a) Temperature, °C

thermal analysis on a special equipment permitting simultaneous recording of the absolute and differential thermal curves. Figure 3, illustrating the differential curve, clearly reveals the onset of solution of the γ-phase at 860°, and the onset of fusion at 1370°. The end of solution of the γ-phase and the moment of final transition of the alloy to the liquid condition was recorded less successfully; however, it may be held, with some error that these temperatures are, respectively, 1180 and 1530°. Inasmuch as the area between the true differential curve and its imaginary position in the absence of transformations (the broken line in Fig.3) is proportional to the heat effect of transformation, it may be observed that the heat effect of solution hardly differs from the position of the heat effect of fusion of the alloy. No anomaly of the type that indicates the existence of a eutectoid transformation is seen here, while, according to

24. (Bibl.16) this alloy is almost precisely of eutectoid composition. Specimens of alloys (containing 30 to 35 wt.% nickel) to be used for Debye x-ray analysis were quenched from temperatures of 1310 - 1320°. A 10% aqueous solution of KOH was the quenching medium. In the control specimens for microanalysis quenched under identical conditions, a coarse granular homogeneous polyhedron structure of solid solution with a hardness of more than 800 kg/mm^2 was found. The x-ray samples were surface-etched to a depth of 0.2 mm, and the pictures were taken in a cylindrical chamber of 57.3 mm diameter, the specimens being rotated in chromium radiation. All the radiographs showed lines only for the solid α-solution with body-centered cubic lattice. Moreover, the α-solution was so coarse-grained that, despite the rotation of the specimen, the lines were not solid.

Fig.3 - Differential Thermal Curve of Alloy with 32.6% Ni in the Annealed Condition

The change in the parameter of the crystal lattice of α - Cr upon solution of nickel therein was also confirmed by x-ray. This was done by quenching alloys containing 10 - 32% Ni from the single-phase region at temperature 1310 - 1320°. The specimen surfaces were roughened and etched, subsequent to which radiographs were taken in a reflection camera with chromium radiation and focusing on the (211) line. The results of measurements of the parameter are presented in Fig.4. The curve of variation of the parameter shows deviation from the additivity law. Extrapolation of the curve to a 40.5% Ni concentration, i.e., to the maximum solubility of nickel and chromium, shows a full fluctuation of the parameter from 2.8783 KX in pure chromium to 2.8560 KX, i.e., by 0.0223 KX. The variation of the parameter found in the present study does not differ much from the data in (Bibl.12).

Measurement of the parameter ~~of the~~ lattice of the α-phase of an annealed alloy containing 32.6% Ni showed XX it to be equal to 2.8783 KX, i.e., not to differ from the parameter of pure chromium within the limits of accuracy of the experiment. This confirms Williams' data (Bibl.13) testifying to the fact that at low temperatures nickel is virtually insoluble in chromium.

To verify the solubility curve, specimens of the alloys were quenched from 1150, 1200, and 1250°. At these temperatures they are in the two-phase region. Measurement of the parameter ~~of the~~ crystal lattice of the α-phase made it possible to determine the solubility of XX nickel in chromium. A curve plotted on these three points and extrapolated (Fig.5) resembles the data due to Williams (Bibl.13). However, in general, solubility is lower particularly at the lower temperatures.

245 Variation in the hardness of the alloy from 32.15 wt.% Ni XXXX in accordance with quenching temperature, adduced in Fig.6, shows that up to a quenching temperature of 1050 - 1100°, the hardness hardly differs from that of the annealed alloy, but thereafter it increases in the quenching temperature interval from 1100° to approximately 1300°, whereupon it remains virtually unchanged thereafter.

XXXXXXX%

Ni at.%

Ni wt.%

Fig.4 - Effect of Nickel upon the Parameter ~~of the~~ Crystal Lattice of α-Chromium

XXXXXXX%x

Ni at.%

Ni wt.%

Fig.5 - Curve of Solubility of Nickel in Chromium:
1 - Our data; 2 - Williams' data (Bibl.13)

Microstructural analysis was performed with microsections manufactured in the usual way and electrolytically etched in a solution of the following composition: 10 cc nitric acid, 5 cc glacial acetic acid, and 85 cc water, at 1.5 volts. The structure of the annealed alloy is so characteristic starting at 32.6% Ni (Fig.8a) that the inclination of some writers to seek a eutectoid transformation in this system is nothing to be surprised at.

The results of dilatometric investigation of the tempering of quenched alloys containing 30 - 40% Ni are of interest. We found that a dilatometer curve of an annealed alloy, for example, at 32.6% (Fig.7) looks quite as it should and has a single point inflection at 820°, apparently corresponding to the onset of solution of the γ-phase. A dilatogram of the same alloy quenched from the single-phase α-region shows, in the 305 - 660° temperature interval, a pronounced increase in length, whereas in the 660 - 850° interval it shows an equally marked reduction in length. A curve taken upon cooling of a tempered specimen does not differ from the curve for the cooling of an annealed specimen. The effect of increase in volume is so great as to exceed all dilatometer effects known to us and observed in the solid state in the course of various phase and structural transformations. Alloys lying, in composition, to the right and left of the 32.6% Ni alloy also yield similar effects after quenching but the particular alloy reveals a maximum volumetric effect. On the chromium side, the
246 diminution in the magnitude of the effect is more rapid. The effect is virtually absent even with a 29.44% Ni alloy. On the nickel side, the diminution is smoother as the effect is still observed with a 39.77% Ni alloy, although it is only weakly to be seen. The effect is strongly affected by quenching temperature. It is still very weak at 1200°, stronger at 1250°, but becomes quite pronounced only at 1310°. In order to clarify the nature of this phenomenon, a number of Debye specimens of the same alloy

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were quenched along with, and under the same conditions, the dilatometer specimen of the 32.6% Ni alloy. The radiograph of the quenched alloy showed, as already noted above, a lattice consisting exclusively of α-phase of very coarse grains. When dilatograms were taken, the x-ray specimens were heated as "witnesses" along with the dilatometer specimens and were quenched in sequence in temperatures that, in our opinion, corresponded to the most characteristic stages of the process (450, 550, 700, and 800°). The radiographs starting with that representing 450° showed lines for the γ-phase, first weak but then (at 550 and 700°) of increasing brightness. The α-phase lines were blurred at 450° and, particularly, at 550° to such an extent that the (211) line completely merged with the background. From 700° on, the washing out of the α-phase lines diminishes and at 800° the radiograph hardly differs from that of an annealed specimen of the same alloy. Judging by the radiographs of tempered specimens, separation of the γ-phase is apparently not coherent with the matrix from the very beginning, inasmuch as only individual spots of α-phase are available, while in the case of coherent separation, the corresponding separate reflection spots of γ-phase would have appeared. In reality, however, separation of the γ-phase yields reflections in the form of solid lines from the very outset.

Fig.6 - Relationship of Hardness of Quenched Alloy with 32.15% Ni to Quenching Temperature
a) $t_{quenching}$, °C

It has thus been established that an increase in volume starting at 305° on the dilatometer

Fig.7 - Dilatometer Records of Alloy with 32.6% Ni Quenched from 1310° and Annealed
a) Quenching from 1310°;
b) Annealing at 1100°

record for the tempering of a quenched alloy is in some manner related to the appearance of a second phase. However, computation of the change in the specific volume that should occur as a consequence of tempering, performed on the basis of x-ray data with respect to changes in parameter and the hypothesis that the phase composition of the tempered specimen is in equilibrium at room temperature, showed that the change in volume should be less in quantity and opposite in sign. As a result of the separation of the γ-phase, the volume of alloy should have been reduced. The anomalous changes in volume upon tempering are as yet unclarified.

The investigation of the chromium-nickel binary system performed permits the conclusion to be drawn that, in this system, eutectoid transformations apparently do not occur. In fact, the rearrangement of the crystal lattice from body-centered to face-centered or to a compact hexagonal lattice should be accompanied by a substantial volumetric effect. If even at a 6000-fold increase this effect does not appear, it is natural to assume that it does not exist. The absence of any anomalies whatever on the differential temperature curve and on the curve for variation of the hardness of alloys quenched from various temperatures in the temperature interval referred to in (Bibl.16) also bears witness to the fact that no phase transformations occur within this interval. This is also confirmed by investigations of changes in the parameter of the crystal lattice of the α-solid solution, which varies monotonically at least to 31.4% Ni, contradicting the diagram illustrated in (Bibl.16). X-ray investigations of quenched and tempered alloys at all concentrations and at quenching temperatures as high as 1380° have not shown any phases other than the α and γ to be present.

Chromium-Nickel-Niobium Ternary System

Fifty-two more alloys in addition to those already mentioned were prepared for investigation of the ternary system. The initial materials were electrolytic chromium purified by annealing in hydrogen, grade 0000 nickel, and briqueted high-purity niobium.

2/ All the alloys were melted in an arc furnace. The method of producing the alloys was the same as that used to get the chromium-nickel binary alloys. The compositions of all the alloys melted are presented in Table 2.

Abrasive stone was employed to remove pieces of the melted alloys for investigation in the cast condition. The ingots were then annealed at a temperature of 1100° for 107 hrs in a purified argon atmosphere. The control of homogenation of the alloys was by x-ray methods, based on the broadening of lines at large angles obtained by x-ray photography in a Saxe camera. Homogenation was regarded as satisfactory when the cleavage K_α doublet, when radiography was performed by chromium radiation, became noticeable.

Pieces were cut from the annealed ingots cooled slowly in the furnace, for investigation of microstructure. Powders of a majority of the alloys were made for x-ray phase analysis either by filing or by crushing in a special mortar made of ~~XXXXX~~ grade KhVG tempered steel. In some cases the alloys were ~~XXX~~ neither filed nor crushed (Nos.35, 36, 52 alloys). Debye specimens were cut from them with considerable difficulty.

The methods of microstructural and x-ray structural analysis, as well as hardness measurement, were employed to investigate the chromium-nickel-niobium ternary system. Microstructural ~~XXXXXXXXX~~ analysis was performed on ~~slides manufactured~~ microsections prepared in the usual fashion. The ~~slides~~ sections were etched electrolytically in the same reactant as the binary chromium-nickel alloy. It was only a few of the alloys that had to be etched in a 1% solution of boiling sulfuric acid in water, while binary alloys of nickel and niobium and alloys containing a small quantity of chromium had to be etched in a reactant consisting of a mixture of 1 part hydrofluoric, 1 part nitric, and 2 parts sulfuric acids with 3 parts water. Microsections ~~XXXXXXXXXX~~ of single-phase alloys in the γ-region were made by electrolytic polishing and etching.

X-ray phase analysis was performed in a cylindrical Debye camera of 57.3 mm diameter.

247 The radiographs were taken in unfiltered chromium radiation employing a rotating specimen.

248 Table 2

Note: The zero in the Table means absence of the element in the alloy, whereas a dash means that analysis for the presence of this element was not performed.

a) Alloy number; b) Chromium content, wt.%; c) Niobium content, wt.%; d) Nickel content, wt.%

In order to indicate the phases, ~~XXXXXX~~ radiographs were taken in advance from four "standards of comparison": chromium, nickel, and the $NbCr_2$ and Ni_3Nb intermetallic compounds. The phases present were identified by simple comparison of the radiograph of the alloy with radiographs of the "standards of comparison". It was found that no phases other than α-chromium, γ-nickel, β-$NbCr_2$, and δ-Ni_3Nb exist in the alloys quenched from 1100°.

In order to construct an isothermic section through a diagram of phase equilibria of the chromium-nickel-niobium ternary system at 1100°, specimens of all the alloys (including binary chromium-nickel alloys) which were to be used to make microsections,

as well as of powders in nickel-foil packages, were placed in evacuated sealed quartz ampules heated in the furnace to 1100°, held for 5 hrs, and quenched in water with breaking of the ampules.

Figure 8 (b,d) illustrates the microstructure of alloy No.51 in the initial, cast condition and in the condition existing after annealing at 1100° for 112 hrs followed by quenching in water. The annealing is carried on until the typical eutectic structure disappears. Figure 8c presents the microstructure of No.7 alloy, which lies in the three-phase $\alpha + \gamma + \delta$ region. Here all three phases are readily visible: the dark γ-phase, the small bright particles of the α-phase, and the δ-phase constituting the remainder of the field, although the latter is strewn with γ-phase precipitations.

Fig.8 - Microstructure of the Alloys (700×)

It has been established, on the basis of the data of x-ray phase analysis that two quasi-binary sections exist in the investigated portion of the chromium-nickel-niobium ternary system: one between the chromium and the Ni_3Nb intermetallic compound and another between the two intermetallic compounds $NbCr_2$ and Ni_3Nb. This derives directly from the

fact that interference lines appear on the radiographs of all the alloys lying along a straight line connecting chromium and Ni_3Nb in the former instance, $NbCr_2$ and Ni_3Nb in the latter, these lines combining to form the given quasi-binary section (either two together or each separately). Moreover, the radiographs of alloys to one side of the chromium-Ni_3Nb line never reveal γ-phase lines, nor are β-phase lines found on the other side. These quasi-binary cross sections divide the triangle of concentration into three parts, each of which may be regarded as an independent ternary system. Each of the ternary systems we investigated (Cr-Ni-Ni_3Nb) and Cr-$NbCr_2$-Ni_3Nb) have a phase equilibrium diagram which, at 1100°, contains intervals of single, double, and triple-phase equilibria (Fig.1).

Summary

1. A eutectoid transformation is apparently lacking in the chromium-nickel system.

2. An anomalous variation in volume occurs when certain alloys of the chromium-nickel system quenched from 1310° are tempered.

3. The boundaries of the phase intervals in an isothermal cross section of the phase diagram of the chromium-nickel-niobium system have been plotted for 1100°.

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