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CHEMISTRY

1962

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Abstract

Full Text

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INVESTIGATION OF THE STRUCTURE OF ALLOYS OF THE NICKEL–CHROMIUM–BORON SYSTEM

(Presented by Academician I. I. Chernyaev, December 28, 1961)

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The literature contains detailed investigations of the phase composition of alloys of the nickel–boron [1] and chromium–boron [2] systems. The phase composition of alloys of the nickel–chromium–boron system containing up to 25% chromium and small amounts of boron is given in [3*]. The present article presents the results of an investigation of the phase composition of alloys of the nickel–chromium–boron system containing 33-50 at.% boron. Pure metals and amorphous boron, obtained by thermal dissociation of diborane and containing not less than 99.5% B, were used for preparing the alloys. Alloys containing more than 0.5% B were obtained by melting, in an atmosphere of pure argon, a pressed charge for which, in addition to boron, carbonyl nickel containing 99.8% Ni, 0.18% C, and 0.02% other impurities, and hydride chromium containing 99.6% Cr, 0.25% Fe, 0.10% Si, and 0.05% Ni were used. The weight of the charge was 20 g. Carbon analysis showed that 0.04-0.05% C remains in the alloys. Alloys containing from 0.15 to 0.3% B were usually melted in an atmosphere of pure argon, and those containing less than 0.15% B–in vacuum.

For preparing these alloys the following were used: nickel of grade H0000 (99.98%), refined chromium (99.94%), and a 4% nickel–boron master alloy containing not more than 0.03% impurities. Alloys containing not very large amounts of chromium and boron were melted in alumina crucibles, and refractory alloys–in zirconium dioxide crucibles. In making up the charge, it was assumed that 5% of the weight of boron is moisture adsorbed by the boron during weighing. Chemical analysis of a number of alloys showed that there is good agreement between the specified and the obtained composition. Before investigation, the alloys were annealed in an atmosphere of pure argon at 1000° for 250 hours, followed by cooling in air. Some alloys were annealed for 100 hours; however, changing the duration of holding during annealing did not lead to noticeable changes in structure.

Determination of the phase composition was carried out by x-ray analysis by the powder method using CrK_α, CoK_α, and CuK_α radiations, and by metallographic analysis with measurement of microhardness on a PMT-3 instrument under a load of 50 g. Powders for x-ray structural analysis of alloys containing more than 10 at.% boron were prepared by grinding specimens in a mortar or by chemical isolation of chromium borides. For alloys with lower boron con-

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Fig. 1. Isothermal section at 1000° of the nickel–chromium–boron system (up to 50 at. % B)

Figure 1: Fig. 1. Isothermal section at 1000° of the nickel–chromium–boron system (up to 50 at. % B)

tent, powders were obtained by electrolytic separation in aqueous or methanolic electrolytes.

The results of the investigation of the phase composition of the alloys are presented in Fig. 1. The solubility of boron in solid solutions based on nickel and based on chromium lies within the range 0.02–0.04 at.%. The regions of the solid solutions γ, $\gamma + \alpha$, α, in accordance with the known phase diagram of nickel –chromium, are shown by arrows on the isothermal section; owing to the low solubility of boron, the line bounding these regions in Fig. 1 almost coincides with the base of the triangle. Analysis of the composition of the borides

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* In work [3] the phase composition of the three-phase region is described correctly in the text, but is shown incorrectly in the figure.

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Fig. 2. Microstructure of an alloy containing 22.5 at. % chromium and 25 at. % boron; 500×

Fig. 3. Microstructure of an alloy containing 47.3 at. % chromium and 30.3 at. % boron; 500×

Fig. 4. Microstructure of an alloy containing 67 at. % chromium and 1.5 at. % boron; 500×

chromium and nickel boride Ni_3B, isolated electrolytically, showed that in the chromium borides formed in alloys with a low boron content, nickel practically does not dissolve; in any case, the solubility of nickel in them does not exceed 0.2 at. %, while chromium practically does not dissolve in nickel boride. Taking into account the narrow range of boron content in the homogeneous chromium and nickel borides, it may apparently be assumed that the β, δ, ε, and θ phases are phases with narrow homogeneity ranges.

Fig. 1. Isothermal section at 1000° of the nickel–chromium–boron system (up to 50 at. % B)

For a more accurate determination of the boundaries of a number of phase regions of alloys containing from 20 to 34 at. % chromium, samples with a low boron content and a small interval of variation in chromium content were melted. The structure of these alloys, depending on chromium content, is characterized by the data given in Table 1.

Table 1

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Phase composition of a series of alloys with a low boron content

Alloy Nos.	Content, at. % B	Content, at. % Cr	Phase composition	Alloy Nos.	Content, at. % B	Content, at. % Cr	Phase composition
1E	2.0	19.8	$\gamma + \theta + \varepsilon$	4E	2.1	28.3	$\gamma + \delta$
2E-1	2.0	21.8	$\gamma + \varepsilon$	5E	2.1	30.4	$\gamma + \delta$
2E	2.0	23.9	$\gamma + \varepsilon$	6E	2.1	32.4	$\gamma + \beta$
3E	2.0	26.1	$\gamma + \delta + \varepsilon$	7E	2.1	34.1	$\gamma + \beta$

Microstructures of a number of alloys of the nickel–chromium–boron system are shown in Figs. 2, 3, and 4.

In Fig. 2 three structural constituents with indentations from a diamond pyramid are clearly visible: a nickel-based solid solution (γ) with the lowest microhardness, chromium boride CrB (ε-phase) with the highest microhardness, and nickel boride Ni_3B (θ-phase).

Figure 3 shows the microstructure of a three-phase alloy $\gamma + \delta + \varepsilon$. In terms of microhardness, the chromium borides differ little from one another. In Fig. 3 the length of the indentation diagonal on crystals of the δ-phase averages $8\,\mu$, which corresponds to a microhardness of 1500 kg/mm^2, while the diagonal length on crystals of the ε-phase averages $7.5\,\mu$, which corresponds to a microhardness of 1700 kg/mm^2. Variations in microhardness on different crystals of different specimens are $\mp$100 kg/mm^2. The microhardness of the β-phase is the same as the microhardness of the ε-phase and averages 1700 kg/mm^2. Thus, for the chromium borides no increase in hardness is observed with incre-

of boron content. The same circumstance was noted by Novotny et al., who investigated alloys of the vanadium–boron system ([4]). The authors observed approximately the same microhardness, $H = 2300$ kg/mm^2, for the vanadium borides V_3B_2 and VB.

Figure 4 shows the microstructure of the three-phase alloy $\alpha + \gamma + \beta$. The chromium-based solid solution has greater hardness and is characterized by a smaller indentation from the diamond pyramid than the nickel-based solid solution. A peculiarity of the phase diagram of alloys of the nickel–chromium–boron system is that in this system, apparently, no ternary intermetallic compounds are formed.

In 1919 Vogel ([5]) noted that the formation of ternary compounds in ternary systems may be expected if in two and, especially, in all three binary systems there is a mutual affinity of the components. The study of nickel alloys with

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chromium and boron, with molybdenum and boron ([6]), as well as of a number of other ternary systems, suggests that in ternary systems nickel–transition metal –boron, ternary phases may form in the case where metallic compounds are present in the binary nickel–metal system. Otherwise, in the nickel–transition metal–boron system only phases based on nickel borides and metal borides will be encountered.

Of practical importance may be the determination of the composition of borides in nickel-chromium alloys with boron and additions of aluminum and titanium.

The introduction into nickel-chromium alloys with boron of small amounts of titanium and aluminum does not lead to the appearance of boride phases different from those present in the nickel–chromium–boron system, but it may affect the structure of the borides formed in these alloys.

Data on the effect of changing the aluminum content on the structure of chromium borides are given for a number of alloys in Table 2.

Table 2

Phase composition of a series of alloys on a nickel-chromium base with boron

Alloy No.	B	Cr	Ti	Al	Structure of chromium boride	Alloy No.	B	Cr	Ti	Al	Structure of chromium boride
132B	0.34	19.1	2.59	0.86	ε (CrB)	148B	0.31	19.6	2.80	2.10	δ (Cr_5B_3)
146B	0.29	21.8	3.30	1.50	δ (Cr_5B_3)	152B	0.22	18.6	2.70	3.25	β (Cr_2B)
151B	0.20	19.7	3.07	1.75	δ (Cr_5B_3)	154B	0.23	24.2	2.70	3.02	β (Cr_2B)

From Table 2 it is evident that the introduction of boron into the nickel alloys used leads to the formation of boride phases, the structure of which depends on the aluminum content.

The author expresses deep gratitude to S. A. Strekopytov, E. M. Alymova, and A. R. Abezgauz, who assisted in carrying out the experimental part of the work.

Air Force Engineering Academy
named after Prof. N. E. Zhukovsky

Received
24 XII 1961

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