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Abstract

Full Text

Chemistry

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Investigation of the Structure of Alloys of the Molybdenum–Nickel–Boron System

(Presented by Academician I. I. Chernyaev, September 13, 1963)

At present, binary systems of metals with boron have been studied quite fully. The phase composition and interaction of components in Me–Me–B systems have been insufficiently studied for many of them; such systems include molybdenum–nickel–boron. For this system, the present article gives the results of a study of the phase composition of alloys containing up to 50 at.% boron.

The binary systems nickel–boron and molybdenum–boron have been investigated by many authors. The phase diagram of the nickel–boron system was first constructed in 1915 ⁽¹⁾ and refined in work ⁽²⁾. The crystal structure of nickel borides has been determined by many authors, and by the present time these investigations have apparently been completed by the author of work ⁽³⁾. Studies of alloys of molybdenum with boron are the subject of works ^(4, 5, etc.), which give data on the phase composition of alloys of the molybdenum–boron system and on the crystal structure of molybdenum borides. A complete bibliography on this system is given in the monograph ⁽⁶⁾. The ternary system molybdenum–nickel–boron is the subject of work ⁽⁷⁾, in which the ternary compound Mo₂NiB₂ is investigated, and of work ⁽⁸⁾, in which the results of a study of the phase composition of nickel-rich alloys of this system are presented.

We investigated, as a rule, the phase composition of cast alloys, and only for alloys rich in molybdenum and boron did we confine ourselves to the study of sintered compositions.

The charge materials used for preparing the alloys were: nickel of grade N0000, containing not less than 99.99% nickel; carbonyl nickel, containing not less than 99.8% nickel; powdered molybdenum, containing not less than 99.7% molybdenum; molybdenum in rods of 99.98% purity; and amorphous boron, obtained by thermal dissociation of diborane, containing not less than 99.5% B.

Alloys containing small amounts of boron and molybdenum were melted in alumina crucibles in a high-frequency installation MVP-3. Alloys containing larger amounts of boron and molybdenum were prepared by thorough mixing of the component powders, pressing them, sintering in a TVV-2 vacuum furnace, and only after this was melting carried out in the MVP-3 installation in zirconia crucibles.

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

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

Chemical analysis of a number of alloys showed that there is good agreement between the specified and the obtained composition.

Before examination, the alloys were annealed in an atmosphere of pure argon at 1000° for 100 hours. To determine the phase composition of the alloys, X-ray analysis was used with $\text{CoK}\alpha$ and $\text{CuK}\alpha$ radiation, as well as microscopic analysis with measurement of microhardness on a PMT-3 instrument under loads of 20 and 50 g.

In studying the microstructure of the alloys, various methods of revealing the structure were used: 1) oxide etching by high-frequency currents; 2) electrolytic etching in the reagent: 1 g H_3PO_4 + 4 g H_2O_2 , anodic etching, electrode–platinum, current density $D = 0.1 \text{ A/cm}^2$; 3) chemical etching in the reagent: 4 g CuSO_4 + 20 cm³ HCl + 76 cm³ H_2O , etching time 3–15 sec.

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Fig. 2

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a

b

c

Fig. 2. Microstructure of alloys:

a –with 10 at. % boron and 87.5 at. % nickel (400×);

b –with 33 at. % boron and 60 at. % nickel (500×);

c –with 15 at. % boron and 20 at. % nickel

Powders obtained by grinding specimens or by separation during anodic dissolution of alloys in a reagent of the following composition were subjected to X-ray analysis: 30% NH_4F + 4% H_2SO_4 + 14% HCl + 52% H_2O . The current density during the electrochemical separation of borides was 0.25 A/cm^2 ; the separation time was three hours. Debye cameras with a diameter of 57.4 mm were used to obtain the X-ray diffraction patterns.

The results of the investigation of the phase composition of the alloys are presented in Fig. 1. The structure of the alloys consists of the following constituents: solid solutions based on molybdenum– α –and on nickel– γ ; the intermetallic compound NiMo–the δ phase; phases based on binary borides; and the ternary phase M, having the composition NiMoB.

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

The designations of phases based on binary borides are as follows: η with the lattice Ni_3B , $\theta\text{-Ni}_2\text{B}$, $\lambda\text{-Ni}_4\text{B}_3$, $\mu\text{-NiB}$, $\beta\text{-Mo}_2\text{B}$, $\epsilon\text{-Mo}_3\text{B}_2$, and ξ based on the compound MoB .

The solubility of boron in solid solutions based on molybdenum and on nickel was not determined in the present work, but on the basis of other investigations it may be assumed that it is small: in the γ phase no more than 0.02 at.% boron dissolves, and in the α solid solution somewhat more. Structures characteristic of alloys of this system are shown in Fig. 2 (see insert, p. 1118).

Figure 2a shows a structure characteristic of the nickel corner of this system. The light constituent of the structure is the η phase with the Ni_3B lattice; the dark constituent is a solid solution based on nickel, with a microhardness of 200–250 kg/mm^2 .

Figure 2b shows a structure characteristic of alloys containing 33 at.% boron. In this case the sharply delineated constituent is the M phase, which is located in the field of the θ phase.

Figure 2c shows the microstructure of a three-phase alloy. The gray crystals are molybdenum boride (β phase), the white ones are the δ phase based on the compound NiMo , and the dark ones are the α solid solution; the dark phase shows large impressions from the diamond pyramid of the PMT-3 instrument.

Along with the investigation of the microstructure, measurements were made of the microhardness of the phase constituents of this system. Phases based on nickel borides have a microhardness in the range 1000–1100 kg/mm^2 ; the microhardness of phases based on molybdenum borides, as well as of the M phase, is 1500–1600 kg/mm^2 .

The microhardness of phases based on nickel borides and phases based on borides of molybdenum, thus, is practically independent of the ratio between the amount of metal and the amount of boron. However, there are data in the literature indicating that the microhardness of boride phases generally increases with increasing boron content.

Apparently, the discrepancies that exist on this question are explained by differences in the method of preparing the boride phases, as a result of which specimens are obtained not only with unequal porosity, but also with different impurity contents.

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