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Abstract

Full Text

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ON THE COMPOUND Ni_3B IN NICKEL–BORON ALLOYS

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The binary phase diagram of Ni–B (up to 20% B) was first constructed by Guertler in 1915 ([1]). Guertler found that the nickel-richest compound in the Ni–B system is Ni_2B. Binet de Chassonne ([2]) isolated this compound in nickel alloys with 5% B. Börstrom ([3]), in an X-ray structural study of a Ni–B alloy, established that the Ni_2B phase (8.44% B) is isomorphous with the phases Fe_2B and Co_2B and has a body-centered tetragonal crystal lattice with parameters: $a = 4.90$ kX, $c = 4.236$ kX. Kiessling ([4]), as a result of an X-ray structural study, indicated the existence in nickel-rich alloys, in addition to the Ni_2B phase, also of the Ni_3B phase, but did not give any data characterizing it.

Table 1

Content of Ni and B in the insoluble residue after heating the alloy with H_2SO_4 (1 : 2) until dissolution ceased

B in alloy, %	Ni in insoluble residue, %	B in insoluble residue, %	Ratio of atomic indices Ni : B
0.19	1.48	0.085	3.2 : 1
0.34	2.48	0.17	2.8 : 1
1.62	13.6	0.76	3.3 : 1
2.27	20.0	1.19	3.1 : 1
2.49	20.8	1.30	3.0 : 1

We investigated the structure and phase composition of Ni–B alloys containing from 0.01 to 2.5% B. The alloys were cast by introducing a Ni–B master alloy containing 5% B.

Metallographic examination of the cast alloys showed that in these alloys along the grain boundaries there separates out a uniformly etched phase, forming a eutectic with nickel. The alloy with 2.5% B is hypereutectic (Fig. 1). We succeeded in isolating this phase both chemically and electrolytically. To isolate the phase by the chemical method, a small quantity of alloy turnings was heated with sulfuric acid (1 : 2) until dissolution ceased.

Table 2

Content of Ni and B in anodic precipitates isolated electrolytically in aqueous electrolytes

B in alloy, %	Electrolyte	Ni in anodic residues, %	B in anodic residues, %	Ratio of atomic indices Ni : B
2.49	1	5.80	0.40	2.7 : 1
2.49	2	10.63	0.62	3.2 : 1
2.49	3	11.84	0.80	2.7 : 1

Note. Composition of electrolytes: **1** –10 g $(NH_4)_2SO_4$, 35 g citric acid, 15 g NH_2OH; **2** –10 g $(NH_4)_2 \cdot SO_4$, 35 g citric acid, 25 g NH_2OH, 1200 ml water; **3** –10 g $(NH_4)_2 \cdot SO_4$, 30 g NH_2OH, 1200 ml water, with cooling.

In electrolytic separation of the phases, a cylindrical alloy specimen was subjected to anodic dissolution under ordinary conditions with aqueous and non-aqueous electrolytes of the following composition: 1) 10 g $(NH_4)_2SO_4$, 30 g hydrochloric hydroxylamine per 1200 ml water, and 2) 50 ml HCl per 1150 ml methanol, with cooling.

The phase isolated by one method or another was subjected to X-ray structural study and chemical analysis.

Figure 2 shows a typical X-ray diffraction pattern obtained from isolated phases using CuKα radiation. Below are the results of an X-ray structural analysis of the Ni_3B phase, carried out by the powder method.

No.	Intensity	d in Å	No.	Intensity	d in Å
1	medium	2.43	21	very weak	1.226
2	strong	2.35	22	medium-strong	1.187
3	medium	2.25	23	strong	1.159
4	strong-medium	2.12	24	medium	1.139
5	very strong	2.035	25	strong	1.123
6	strong	1.96	26	medium	1.106
7	strong	1.94	27	medium-weak	1.076
8	very strong	1.85	28	very weak	1.032
9	medium-strong	1.74	29	weak	1.001
10	medium	1.68	30	very strong	0.9679
11	very weak	1.64	31	very weak	0.2509
12	medium	1.62	32	weak	0.9298
13	weak-medium	1.57	33	medium	0.9242
14	weak-medium	1.44	34	weak	0.8632
15	weak	1.40	35	strong	0.8551
16	weak	1.38	36	weak	0.8413

No.	Intensity	d in Å	No.	Intensity	d in Å
17	weak	1.335	37	strong	0.8274
18	strong	1.294	38	strong-medium	0.8240
19	strong-medium	1.250	39	strong	0.8163
20	weak	1.232	40	strong-medium	0.8041

The results of chemical analysis of the phases isolated from the alloy by various methods are given in Tables 1-3, in which the analysis results are calculated relative to the weight of the dissolved alloy.

From the data given in Tables 1-3 it is evident that, in electrolytic separation of the phases, a considerable portion of nickel boride dissolves; the greatest amount of it is retained when the alloy is treated with sulfuric acid (1 : 2). In all cases the precipitate, according to X-ray structural investigation, represented one and the same phase. According to the results of chemical analysis, the composition of the isolated phase may be represented as Ni_3B.

Table 3

Content of Ni and B in anodic precipitates isolated in an anhydrous electrolyte (50 ml HCl (1.19) per 1150 ml CH_3OH) under strong cooling

B in the alloy, %	Ni in the anodic precipitate, %	B in the anodic precipitate, %	Ratio of atomic indices Ni : B
0.19	0.077	0.005	2.7 : 1
0.34	0.230	0.016	2.6 : 1
2.49	0.96	0.066	2.7 : 1

This nickel boride is a hard black substance. It is insoluble in dilute sulfuric acid (1 : 2). In concentrated sulfuric acid (1.84) it dissolves upon prolonged heating. In concentrated hydrochloric acid (1.19), and also in dilute hydrochloric acid (1 : 1), it dissolves only slightly upon prolonged boiling. In dilute nitric acid and in aqua regia it dissolves in the cold. It also dissolves readily in dilute hydrochloric and sulfuric acids in the presence of oxidizing agents—hydrogen peroxide, persulfate, etc.

Thus, on the basis of the investigation carried out, it may be asserted that in the binary Ni—B system there exists the chemical compound Ni_3B, forming a eutectic with the solid solution based on nickel.

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Fig. 1

Fig. 2

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Note: Figure translations are in progress. See original paper for figures.