V. T. Serebryanskii, V. A. Epel'baum, and G. S. Zhdanov

1961

SovietRxiv

Fig. 1. Phase diagram of the aluminum–boron system. Dashed line: 1 –Xenny' s data with additions by Füs and Meissner, 2 –Hofman and Enikhe' s data. Solid curve –our data

Figure 1: Fig. 1. Phase diagram of the aluminum–boron system. Dashed line: 1 –Xenny' s data with additions by Füs and Meissner, 2 –Hofman and Enikhe' s data. Solid curve –our data

Abstract

Full Text

V. T. Serebryanskii, V. A. Epel' baum, and G. S. Zhdanov

On the Phase Diagram of the Aluminum–Boron System

(Presented by Academician N. V. Belov, July 11, 1961)

The first systematic investigation of the aluminum–boron system was carried out by Xenny ([1]) in 1925, who studied thermographically aluminum alloys with boron, with a boron content up to 8.5 wt.%, and found a eutectic at 565°. Its composition, by extrapolation, lay in the region of 15-18% boron.

Fig. 1. Phase diagram of the aluminum–boron system.
Dashed line: **1** –Xenny' s data with additions by Füs and Meissner, **2** –Hofman and Enikhe' s data. Solid curve –our data.

Füs ([2]) and Meissner ([3]) extrapolated the liquidus curve to 50% (Fig. 1). Hofman and Enikhe ([4]), in 1936, using microscopic and X-ray methods, found a eutectic at 0.2% boron and 658°. They also established a strong increase in the melting point of aluminum with increasing boron content up to 4% B and a peritectic horizontal at 1350°. The high melting temperature of the alloys did not allow the authors to carry out further study of the diagram. According to ([1]), the phase AlB_2 decomposes at 1100°; according to ([4]), it is formed as the result of a peritectic reaction at 1350°. AlB_{12} crystallizes in several modifications ([5,6]), the conditions of existence of which have not yet been the subject of study. Kohn, Katz, and Giardini ([7]) discovered one more phase, corresponding to the composition AlB_{10}.

The far from complete and contradictory data on the phase diagram, as well as the practical importance of aluminum-boride phases as semiconductors ([8]) and abrasives ([9]), make clear the necessity of further investigations in this system.

Experimental Method

To investigate the phase diagram, we assembled an installation for high-temperature contactless thermal analysis, VNTA-1, designed by N. A. Nedumov ([10]), which makes it possible to carry out thermal analysis up to 2800° C. Samples in the form of pressed rods weighing 5 g were prepared from aluminum of 99.99% purity and boron of 99.5% purity (0.16% H, 0.26% O). Placed in crucibles made of corundum or BeO, they were brought to melting in an atmosphere of purified helium and then cooled together with the furnace at a rate of 20 deg/min. Recording was performed both as ordinary and differential. For alloys containing more than 50% boron, only

heating, since the crucibles reacted somewhat with the sample after it had been melted.

All phases obtained in pure form were analyzed for aluminum and boron; their pycnometric density was also determined. Some of the alloys were subjected to chemical analysis after thermographic investigation. The results of the analyses showed that the difference between the specified and the obtained composition was $±0.3 $ and Cu Kα radiation in cameras 86 mm in diameter, with asymmetric loading of the film.

Results of the investigation

The general form of the phase diagram is shown in Fig. 1, from which it is seen that the phase diagram of the aluminum—boron system is a complex system that includes a number of peritectoid transformations. The initial course of the liquidus curve is the same as in Hoffmann and Jäniche, but the curve itself lies somewhat lower. The lattice constant of aluminum, calculated from the (420) reflection, is 4.041 kX, and for aluminum alloys with boron it is 4.040 kX. Thus the change in the lattice period of aluminum lies within the experimental error. Therefore, on the basis of the X-ray data, no conclusion could be drawn about the solubility of boron in aluminum. The authors of work (4) arrived at the same conclusion. Only a certain broadening of the lines at large angles was observed. In samples containing up to 1% B, aluminum and AlB_2 are present. At a higher boron content in the alloys, along with AlB_2, α-AlB_{12} is also present. The eutectic temperature agrees with the data of (4).

The peritectic line at 975° corresponds to the decomposition

$$AlB_2 \rightarrow AlB_{12} + Al.$$

However, at lower temperatures the alloys are evidently highly nonequilibrium, since in them we find α-AlB_{12}, the amount of which increases with increasing boron content. The compound AlB_2 crystallizes in the form of thin hexagonal plates of bronze color. The lattice parameters are $a = 3.01$ Å, $c = 3.26$ Å. The measured pycnometric density is 3.09 g/cm^2.

In samples quenched from temperatures of 1000-1400°, we found Al and α-AlB_{12} —the tetragonal modification of "graphite-like boron."

As is seen from Fig. 1, the liquidus line on the aluminum side rises steeply upward. At a composition of 11% B it forms an inflection and gives rise to a peritectic horizontal at 1450°. Evidently this is the same horizontal that was found by Hoffmann and Jäniche (4) at 1350°, especially since Lihl and Jänichek (11) indicate for it a temperature higher than 1400°. Several samples with boron contents of 13, 15, 20, and 35% were quenched from 1500°. After dissolution of the aluminum in hydrochloric acid, thin bronze-colored plates were obtained, outwardly resembling AlB_2. Their powder pattern coincides almost exactly with the X-ray pattern of AlB_2, except for several weak lines. Because of impurities it was not possible to carry out chemical analysis or determine the density of this product. Thus, the nature of the transformations at 1450° has not yet been established.

The peritectic at 1550° corresponds to the formation of β-AlB_{12}– "diamond-like boron." In samples with various boron contents up to 82.5%, quenched from 1600°, we obtained this phase in pure form. It crystallizes in the form of long tetragonal prisms or bipyramids. The color ranges from yellow to brown. The lattice parameters agree with the data of Naray-Szabó (6). The measured pycnometric density is 2.60 g/cm^3. It should be noted that Naray-Szabó found carbon in the product he investigated and represented this phase as $C_2Al_3B_{44}$ or $3AlB_{12} \cdot 2B_4C$. We did not carry out an analysis for carbon. However, the syntheses were conducted under conditions excluding contamination by carbon; moreover, the starting products were of high purity.

and chemical analysis of the pure phase gave 82.98% B and 16.85% Al (sometimes the composition differed from the stoichiometric one; for example, for one of the specimens we obtained 86.0% B and 14.1%). Evidently, the carbon detected by Naran-Sabo was present as an impurity introduced either through the starting material or during the aluminothermic reaction. According to our diagram, the temperature range of this phase is 1550-1660°. On slow cooling it transforms into α-AlB_{12}. If, however, the specimen is cooled slowly but not sufficiently sharply, the transformation β-$AlB_{12} \rightarrow \alpha$-$AlB_{12}$ does not have time to go to completion; then, under a binocular magnifying glass, one can see needle-like yellow prisms with black edges, which indicates that the peritectic reaction has not proceeded completely.

In specimens quenched from 1700-1750°, we found AlB_{10}, discovered by Kohn, Katz, and Giardini ([7]). This phase is obtained in the form of black pyramidal crystals. The pycnometric density is 2.72 g/cm^3. The boron and aluminum contents are, respectively, 79.8 and 19.8%. The temperature range is 1660-1850°. On slow cooling, AlB_{10} in the corresponding specimens transforms into α-AlB_{12}. Quenching from temperatures of 1850-2070° and slow cooling of a composition of 82.5% B and 17.5% Al gives α-AlB_{12}. The lattice periods are $a = 10.15$ Å, $c = 14.29$ Å. The measured pycnometric density is 2.62 g/cm^3. The α-AlB_{12} phase is found in alloys with a content of 82.5-93% B. According to the phase diagram, it is a solid solution of aluminum in boron. This fact is also confirmed by the existence of a recently discovered tetragonal modification of boron ([12]), for which the unit-cell parameters are very close to the parameters of α-AlB_{12}.

In order to check the thermal-analysis data, a series of specimens was prepared by arc melting in a helium atmosphere. Specimens of the following compositions were melted: 1) 70% B, 30% Al, 2) 75% B, 25% Al, 3) 80% B, 20% Al, 4) 82.5% B, 17.5% Al, 5) 86% B, 14% Al, 6) 91% B, 10% Al, 7) 96% B, 4% Al, 8) amorphous boron of 99.5% purity.

Chemical analysis showed that the alloys differed somewhat in composition from the specified charge because of partial evaporation of aluminum and boron. Specimens with a boron content of approximately up to 82% consisted of aluminum and α-AlB_{12}. In the concentration interval from 82 to 93% B, only α-AlB_{12} was present in the specimens. Boron melted in the arc furnace proved to be rhombohedral. The parameters of the hexagonal cell, measured from reflections at angles of 78°7′ and 78°58′, are: $a = 10.95$ Å, $c = 23.76$ Å, which agrees with the data ([13]).

In the concentration range from 93 to 100% boron, only one phase was found —the above-mentioned rhombohedral boron; moreover, for an alloy containing 93% B its unit-cell parameters proved to be $a = 10.95$ Å, $c = 23.87$ Å. Thus, the period c increased by 0.11 Å, which is evidently connected with the formation of a solid solution of aluminum in boron.

Physicochemical Institute
named after L. Ya. Karpov

Received
11 VII 1961

CITED LITERATURE

1. P. Haenni, Rev. Met., **23**, 342 (1926).
2. V. Fuß, *Metallographie des Aluminiums und seiner Legierungen*, Berlin, 1934.
3. K. L. Meissner, Zs. Metallkunde, **18**, 324 (1926).
4. W. Hofmann, W. Jäniche, Zs. Metallkunde, **28**, 1 (1936).
5. F. Halla, H. Weil, Zs. Kristallogr., **101**, 435 (1939).
6. S. Naray-Szabo, Zs. Kristallogr., **94**, 367 (1936).

7. J. A. Kohn, G. Katz, A. A. Giardini, Zs. Kristallogr., **111**, 53 (1958).
8. J. Lagrenaudie, J. Chim. phys. et phys.-chim. biol., **52**, 34 (1955).
9. P. Cotter, Am. Mineralist, **43**, 781 (1958).
10. N. A. Nedyumov, ZhFKh, **34**, 184 (1960).
11. F. Lihl, P. Jenitschek, Zs. Metallkunde, **44**, 414 (1953).
12. C. P. Talley, S. La Placa, B. Post, Acta crystallogr., **13**, 271 (1960).
13. D. E. Sands, J. L. Hoard, J. Am. Chem. Soc., **79**, 5582 (1957).

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