P. T. Kolomytsev

1960

SovietRxiv

Abstract

Full Text

P. T. Kolomytsev

PHASE DIAGRAM OF Co–Co_2B

(Presented by Academician I. I. Chernyaev, September 7, 1959)

The phase diagram of the cobalt–boron system that is known at present has been constructed up to 9.87% B on the basis of experimental investigations by N. P. Chizhevsky and B. A. Shmelev (^{1}), independently of the work of Koster and Mulfinger (^{2}), who constructed the phase diagram of the Co–Co_2B system.

The diagram of Koster and Mulfinger is a diagram with one eutectic, having a melting temperature of 1102° and containing 5.5% boron. The solubility of boron in cobalt at the eutectic temperature, according to the authors of work (^{2}), is about 1%. The phase diagram of the cobalt–boron system of N. P. Chizhevsky and B. A. Shmelev, shown in Fig. 1, was constructed on the basis of thermal-analysis data for alloys containing from 0.07 to 9.87% boron. The authors determined the hardness and specific gravity, and also carried out X-ray structural and metallographic investigations of alloys of the cobalt–boron system.

The solubility of boron in cobalt, according to the authors of work (^{1}), is approximately 0.5% (between 0.23 and 0.67%). The authors of works (^{1},^{2}) believed that the first intermetallic phase on the cobalt side in the cobalt–boron system is the compound Co_2B.

Since we (^{3}) established the existence in the cobalt–boron system of the compound Co_3B, not observed by other investigators, it became necessary to refine the phase diagram of this system.

To construct the diagram, specimens with a boron content from 2 to 8.7% were studied in detail, and, in order to judge the solubility of boron in cobalt, down to 0.1% (by charge).

For the preparation of alloys containing from 2 to 8.7% boron, powdered cobalt of 99.53% purity was used, with impurities (in percent): Ni 0.19; Cu 0.01; Fe 0.08; O_2 0.08; C 0.02; Si 0.02; moisture 0.03, and amorphous boron.

The boron was obtained by thermal dissociation of diborane and contained, as impurities, 0.18% hydrogen, 0.826% oxygen, and traces of metals. Hydrogen and oxygen were removed by calcination at 1300-1400° in a vacuum of 10^{-2}-10^{-3} mm. After calcination, the boron content in the powder was not less than 99.8%. The boron and cobalt powders were thoroughly mixed in the corresponding proportions, pressed, and then melted in alumina crucibles. The weight of the charge was 40 g.

Fig. 1. State diagram of the Co–B system (after Chizhevsky and Shmelev)

Figure 1: Fig. 1. State diagram of the Co–B system (after Chizhevsky and Shmelev)

The use of high-quality boron makes it possible to obtain alloys whose composition corresponds well to the charge. Chemical analysis of alloys with 4.0, 5.8, and 8.5% boron, carried out by L. N. Kugai at the Institute of Cermets and Special Alloys of the Academy of Sciences of the Ukrainian SSR, showed that the boron content in the alloys differs from its content in the charge by no more than $±$0.1%. Determination of the temperatures of the beginning and end of crystallization of the alloys was carried out by the method of thermal analysis. The casting was crushed, and small pieces of the alloy were placed in a crucible with an inserted platinum-platinum-rhodium thermocouple. The calibration curve of the thermocouple and galvanometer was checked against nickel grade N0000, whose melting temperature was taken as 1453°, and against alloys with known melting temperatures.

Copper-aluminum eutectic alloy with 8.5% aluminum, having a crystallization temperature of 1037°, and nickel-aluminum eutectic alloy with 13% aluminum, solidifying at 1385°, were used as reference alloys. The primary melting and the subsequent heating and cooling operations necessary for constructing cooling curves were carried out in a vacuum of 10^{-2}–10^{-3} mm. The cooling rate in the upper temperature range did not exceed 25° per min; in the lower range it was considerably lower. The galvanometer readings were recorded every 10 sec. The error in determining the temperature of the critical points did not exceed ±3°. The duration of crystallization of the eutectic alloy averaged 4 min. The results of the thermal analysis are given in Table 1.

Fig. 1. State diagram of the Co–B system
(after Chizhevsky and Shmelev)

Construction of the Tamman triangle from the thermal-analysis data and investigation of the microstructure make it possible to assume that the boron concentration in the eutectic is approximately 4%.

Determination of the crystallization temperature of the eutectic was also carried out by the metallographic method. It turns out that, after holding for one hour at 1095°, in the structure of a previously deformed alloy containing 0.2% boron, a boride constituent melted along the grain boundaries is observed (Fig. 2). As the results of analysis of the boride phase electrochemically isolated from a number of alloys showed, the compound Co_3B apparently is the first boride phase on the cobalt side.

Table 1

Results of thermal analysis of alloys of the Co–B system

Figure 2

Figure 2: Figure 2

Figure 4

Figure 3: Figure 4

Alloy No.	Boron content, wt.%	Start of crystallization: galvanometer reading, mV	Start of crystallization: temp., °C	End of crystallization: galvanometer reading, mV	End of crystallization: temp., °C	Alloy No.	Boron content, wt.%	Start of crystallization: galvanometer reading, mV	Start of crystallization: temp., °C	End of crystallization: galvanometer reading, mV	End of crystallization: temp., °C
K44	2.0	–	–	11.6	1095	K32	5.8	12.8	1185	11.8	1110
K45	3.0	12.20	1140	11.6	1095	K33	6.1	12.8	1185	11.8	1110
K46	3.5	12.03	1125	11.6	1095	K43	7.0	13.4	1230	11.75	1105
K47	3.7	–	–	11.6	1095	K34	7.5	13.7	1255	11.8	1110
K48	4.0	–	–	11.6	1095	K35	8.0	13.8	1260	11.8	1110
K49	4.5	11.8	1110	11.7	1100	K36	8.3	13.8	1260	11.80	1110
K50	5.0	12.05	1127	11.75	1105	K37	8.5	13.85	1265	–	–
K51	5.8	12.6	1170	11.8	1110	K38	8.7	13.9	1270	–	–

In particular, from the hypoeutectic alloy K45, containing 3% boron, the boride phase was electrochemically isolated by the method proposed by N. M. Popova and A. F. Platonova for isolating borides from nickel alloys (^{4}).

As the electrolyte, a 25% aqueous solution of hydrochloric acid with the addition of 3% ammonium fluoride was used. The current density was 0.02 A/cm^2 and higher; the duration of electrolysis was 4 h. X-ray structur-

To the article by P. T. Kolomyitsev, p. 767.

Fig. 2. Microstructure of an alloy containing 0.2% B after one-hour holding at 1095°

Fig. 4. Microstructures of alloys containing: **a** –5% B; **b** –6.1% B

To the article by A. A. Kolosova, p. 936.

Fig. 4. General view of the scar of the heart wall 60 days after the operation. Van Gieson. Approx. 7, ob. 8×

Figure 4

Figure 4: Figure 4

Fig. 3. Phase diagram of the Co—Co_2B system

Figure 5: Fig. 3. Phase diagram of the Co—Co_2B system

structural analysis of the precipitate, carried out by the powder method using CuKα radiation, showed that the boride phase in the alloy with 3% boron is the compound Co_3B.

This circumstance, together with the results of the microstructure study, makes it possible to establish that the structure of hypoeutectic alloys at temperatures above 400° consists of a solid solution based on β-cobalt and the eutectic (β + Co_3B).

Determination of the solubility of boron in cobalt at a temperature close to the eutectic was carried out only by studying the microstructure of specimens containing small amounts of boron. For this purpose, alloys with boron additions (by charge) of 0.010; 0.020, etc., up to 0.10%, were melted in vacuum.

For the preparation of these alloys, charge cobalt of grade K000, containing not less than 99.9% cobalt, and a 4% cobalt—boron master alloy, prepared from powdered cobalt and amorphous boron by the same method as the specimens for thermal analysis, were used.

Fig. 3. Phase diagram of the Co—Co_2B system

The ingots were forged into rods 10 mm in diameter, from which a layer 1-1.5 mm thick was removed on a lathe, and then specimens 25-30 mm long were cut. The latter were subjected to a 30-hour holding at 1080-1090° in an atmosphere of pure argon, followed by cooling in water.

During heat treatment, boron burns out from the surface layers of the specimens most intensively in an ordinary atmosphere, to a lesser extent in an argon atmosphere, and least of all during heat treatment in a good vacuum. In this connection, for preparing metallographic polished sections the end face of a cylindrical specimen was used, from which, before polishing, a layer approximately 3 mm thick was cut off.

From the inner part of the heat-treated specimens, turnings were taken for determining the boron content in the alloys, which was found by the colorimetric method.

Study of the microstructure of the heat-treated specimens makes it possible to consider that the limiting solubility of boron in cobalt at the eutectic temperature is not more than 0.03%.

It should be noted that the method of determining the solubility of boron by diffusion saturation of the metal with subsequent holding at a temperature close to the eutectic, and analysis of the boron content in the solid solution (as was done by Nicholson (5) in determining the solubility of boron in iron), is not entirely suitable for the present system, since it is difficult to obtain, at the boundary with the borided layer, the structure of a homogeneous solid solution without inclusions of the boride phase.

When the surface layer of a cylindrical specimen of cobalt K000 is saturated with boron, even at 700° penetration of boron is observed predominantly along the grain boundaries, with formation of borides elongated toward the center of the polished section. Holding at higher temperatures leads to intens—

···slow diffusion of borides along grain boundaries, reaching the middle of a specimen 8 mm in diameter after 12-16 hours at 1000°.

On the basis of the results obtained, we constructed a phase diagram of the cobalt—boron system up to 8.5% B (Fig. 3).

This diagram differs from the diagram in works [1] by the presence of the compound Co_3B and a peritectic reaction at 1110°.

The inaccurate construction of the diagram by the authors of works [1] and [2] may be explained by the use of insufficiently pure components, by the difficulties of obtaining good X-ray diffraction patterns from polished sections, and by the very slow course of the peritectic reaction in the cobalt—boron system.

Figure 4 shows microphotographs of alloys K50 and K33, containing respectively 5 and 6.1% boron, after cooling in a vacuum furnace with the heater switched off. Under such cooling, both alloys have nonequilibrium, essentially identical three-phase structures consisting of a light constituent—the compound Co_2B, a dark constituent—Co_3B, and a eutectic.

This conclusion regarding the structure is in agreement with the data of X-ray structural analysis.

The microstructure was revealed by electrolytic etching in a solution of $KMnO_4$. When a 10% solution of nitric acid, which was used by the authors of work [1], is employed as the etching reagent, it is not possible to distinguish the compounds Co_2B and Co_3B in the structure. The equilibrium structure of rapidly cooled alloys can be obtained by prolonged annealing at 1000°.

As a result of the investigations carried out, the existence of the compound Co_3B has been established, the maximum solubility of boron in cobalt has been determined, and a new diagram of the $Co—Co_2B$ system has been constructed.

The author expresses deep gratitude to Prof. I. I. Kornilov for his interest in the work, and to E. M. Alymova and A. R. Abesgauz for assistance in carrying out the experiment.

Air Force Engineering Academy
named after N. E. Zhukovskii

Received
2 IX 1959

REFERENCES

[1] N. P. Chizhevskii, B. A. Shmelev, *Tr. Moskovsk. inst. stali im. I. V. Stalina*, **17**, 3 (1940).
[2] W. Köster, U. W. Mulfinger, *Zs. Metallkunde*, **30**, 348 (1938).
[3] P. T. Kolomytsev, DAN, **124**, No. 6, 1247 (1959).
[4] P. T. Kolomytsev, N. V. Moskaleva, S. A. Strelnitsov, *Sborn. nauchn. statei po zharoprochnym splavam*, Moscow, issue 734 (1958).
[5] M. E. Nicolson, *Trans. Am. Inst. Mining Metal. Eng.*, **200**, 185 (1954).

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