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Abstract

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PROPERTIES OF TERNARY ALLOYS OF TITANIUM, CHROMIUM, AND ZIRCONIUM DIBORIDES

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Borides of refractory rare metals, distinguished by high hardness, wear resistance, and resistance to oxidation in various aggressive chemical media, are of substantial interest for modern technology involving high mechanical loads at elevated temperatures. Of particular importance is the study of the properties of boride alloys in systems in which, as in systems of other metal-like compounds (carbides, nitrides), extrema of properties—hardness, electrical resistance, etc.—may be expected. By the present time the results of studies of a number of binary diboride systems have been published: TiB_2—ZrB_2 ([1],[2]), TiB_2—CrB_2, ZrB_2—CrB_2 ([3]), and others.

However, data on the properties of ternary boride alloys are almost entirely lacking, including those of such technically most promising borides as those of titanium, zirconium, and chromium. In this connection, the aim of the present work was to clarify certain properties of alloys of titanium, zirconium, and chromium diborides located on the radial section TiB_2—CrB_2 (50 : 50 mol. %) —ZrB_2.

According to ([1]-[3]), it is known that the borides of titanium and chromium, as well as of titanium and zirconium, form continuous series of solid solutions, while the borides of chromium and zirconium dissolve in one another (at 2000°) only to a limited extent: in CrB_2 up to 20 mol. % ZrB_2 and in ZrB_2 up to 5 mol. % CrB_2. It was therefore of interest simultaneously to follow how the solubility of CrB_2 changes in the solid solution TiB_2—CrB_2 in comparison with its limited solubility in CrB_2 and continuous solubility in TiB_2, and vice versa.

For the preparation of alloy specimens we used the method of sintering by hot pressing, which makes it possible to obtain fairly dense compact specimens from nonplastic, brittle compounds of the boride type. Sintering was carried out in graphite press molds; the investigation of sintering conditions was conducted within temperature limits from 2100 to 2550°, pressures from 60 to 330 kG/cm^2, and holding times from 0.5 to 5 min.

The presence of a minimum at 40-50 mol. % ZrB_2 in the alloys was established on the curve of optimal sintering temperatures; this indicates the absence of a continuous series of solid solutions in the system and the presence of a more

Fig. 2. Change in lattice periods of (Ti, Cr)B_2-ZrB_2 alloys as a function of composition

Figure 1: Fig. 2. Change in lattice periods of (Ti, Cr)B_2-ZrB_2 alloys as a function of composition

complex type of phase diagram.

To relieve internal stresses after sintering by hot pressing, and also to fix the phase state of the alloys, the latter were subjected to annealing in vacuum at temperatures of 1900, 1500, and 1100° with subsequent with rapid cooling to room temperature. The annealed samples were studied by X-ray, metallographic, and microdurometric methods.

Photographs of microsections of a series of alloys, annealed and quenched from 1900°, are shown in Fig. 1. Up to 40-50% ZrB_2 the alloys are single-phase; beginning with 50-60% ZrB_2 a second phase begins to appear, which is visible on the microsection of the alloy with 60 mol.% ZrB_2 in the form of rather fine constituents, and on the microsections of the alloy with 80% ZrB_2—in the form of large inclusions.

Measurement of the microhardness of the phases shows the presence of a maximum microhardness of 3900 kg/mm^2 at 20 mol.% ZrB_2, after which there follows an approximately linear course of the microhardness of the principal phase (2800 kg/mm^2). The hardness of the second phase can be measured with sufficient reliability only beginning with 70 mol.% ZrB_2 in the alloys; it increases from 1900 for ZrB_2 to 2100 kg/mm^2 for solutions in it of the double boride (Ti, Cr)B_2.

Fig. 2. Change in lattice periods of (Ti, Cr)B_2-ZrB_2 alloys as a function of composition

X-ray investigation of the alloys, performed by the Debye method in a normal camera of diameter 57.4 mm, showed (Fig. 2) an increase in the lattice period of the phase based on (Ti, Cr)B_2 with increasing ZrB_2 content in alloys up to 40 mol.%, after which the lattice period of the solid solution of ZrB_2 in (Ti, Cr)B_2 remains practically constant and, beginning with 60 mol.% ZrB_2, zirconium boride—or, more precisely, a solid solution of (Ti, Cr)B_2 in ZrB_2 with a lattice period somewhat smaller than that of pure ZrB_2—is observed on the X-ray diffraction patterns. Determination of the electrical resistivity of the alloys showed the presence of a low maximum at 10 mol.% ZrB_2 in the alloy with (Ti, Cr)B_2. The specific electrical resistivity of ZrB_2 and (Ti, Cr)B_2 is, respectively, 10.8 and 18.8 μΩ/cm.

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Fig. 3. Microbrittleness of the phases TiB_2, CrB_2, and the solid solution (Ti, Cr)B_2

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Thus, it may be assumed that at 1900° the solubility of ZrB_2 in (Ti, Cr)B_2 is of the order of 40 mol.% and the solubility of (Ti, Cr)B_2 in ZrB_2 is less than 10 mol.%; moreover, since the atomic radius of zirconium is larger than the atomic radii of titanium and chromium, the increase in the period upon formation of the first of these solutions indicates dissolution by substitution, and of the second—by interstitial dissolution.

The limited solubility of ZrB_2 in the double boride (Ti, Cr)B_2 is natural, but nevertheless it rises to 40 mol.%, which may be explained by the influence of TiB_2, which forms a continuous series of solid solutions with ZrB_2.

The alloys studied are of interest in that one of the components (ZrB_2) has in the other, (Ti, Cr)B_2, a solubility that changes little with temperature over a wide interval from 1100 to 1900°.

Consequently, in accordance with the principles of designing heat-resistant alloys (*), one may expect, for an alloy with a ZrB_2 content somewhat greater than 40%, the precipitation of excess zirconium boride in the form of a finely dispersed constituent along grain boundaries, preserved at high temperatures and providing high resistance of the entire alloy to creep. At the same time, the main component of the alloy—the solid solution (Ti, Cr)B_2—is formed according to the principle of alloying the more corrosion-resistant, but also more brittle, titanium boride with the less brittle chromium boride ([5], [6]), as is shown by comparison of the microbrittleness of these three phases (Fig. 3).

Conclusions

The solubility of ZrB_2 in $(Ti, Cr)B_2$ is about 40 mol.%, while that of $(Ti, Cr)B_2$ in ZrB_2 is less than 10 mol.%. The solubility range of ZrB_2 in CrB_2 increases when ZrB_2 is dissolved in the binary boride $(Ti, Cr)B_2$, one of whose components, TiB_2, forms a continuous series of solid solutions with zirconium boride.

In the single-phase region of the solid solution of ZrB_2 in $(Ti, Cr)B_2$, in specimens quenched from 1900°, there is a maximum in microhardness of 3900 kg/mm^2 (at 20 mol.% ZrB_2) and in electrical resistivity (216 $\mu\Omega$/cm at 10 mol.% ZrB_2).

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