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Abstract

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PHASES OF THE TUNGSTEN–BORON SYSTEM

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CHEMISTRY

In the x-ray investigation of the tungsten—boron system, three borides were initially found—tetragonal W B and WB, and also hexagonal W B (1). Later studies established the existence of a high-temperature modification of tungsten monoboride, -WB (2, 3). According to (1), W B (-phase) has very narrow homogeneity limits, WB (-phase) has broader limits from 48 to 51 at. % boron (WB . – .), and W B (-phase), in its usual defective state, is homogeneous within the range from 66.7 to 68.0 at. % boron (WB . – .). The phase WB established earlier in ( ) is evidently identical with W B with a deficiency of boron atoms.

In order to refine the phase regions of the tungsten—boron diagram, we* carried out a study of alloys of this system by methods of microhardness, x-ray, and metallographic analyses. For the preparation of alloys, tungsten powder with a content of 99.93% W (96% of grains < 3) and a preparation with the nominal formula WB . , prepared by the vacuum-thermal method ( ) in attempts to obtain WB alloys with x > 5/2, were used. The sum of the boron and carbon contents in this preparation is close to 100%. Mixtures W + WB . were compounded with the calculation of preparing samples with the nominal formulas WB (where x = 0.01; 0.02; 0.05; 0.1; 0.2; 0.4; 0.8; 1.0; 1.5; 2.0; 2.5; 3.0) and were sintered by hot pressing followed by prolonged annealing at 1900° and cooling from this temperature over ~10 h. After determination of the apparent specific gravities and hardness and study of the microstructure, the sintered samples were ground into powder and subjected to chemical and phase x-ray analysis. The results obtained are given in Table 1.

The chemical composition of the alloys (see Table 1) practically did not change during sintering, with the exception of samples charged for WB and the sample WB . , in which the boron content decreased somewhat. The samples obtained upon sintering are sufficiently dense, and after annealing the density of most of them practically does not change or increases slightly; the exceptions are samples WB . , WB . , WB . , WB . , WB , and WB . , upon annealing of which the density decreases rather sharply. This can be explained in accordance with the indication of Raub and Plate ( ), according to whom the effect of spreading forces (“crystallization pressure”) in the formation of intermetallic compounds is caused by the individual separation of newly forming particles.

Investigation of the microstructure of the samples showed that, already beginning with a boron content of 0.9 at. %, two phases are found on polished sections: one of them, light (“white phase”), occupies the main area of the polished section; the second, darker (“gray phase”), is located along the boundaries of the polyhedra of the white phase. With an increase in boron content, the amount of gray phase increases, and

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* S. D. Krasenkova took part in the work.

Table 1

Properties of alloys of the W–B system

Calculated composition, WB_x	B, wt. %	B, at. %	Actual B content in alloy, wt. %	Calculated specific gravity	Specific gravity after hot pressing	Specific gravity after annealing	Microhardness, kg/mm² “white phase”	Microhardness, kg/mm² “gray phase”	Phase composition	Lattice periods of phases, Å: W	Lattice periods of phases, Å: W_2B	Lattice periods of phases, Å: WB	Lattice periods of phases, Å: W_2B_5
W	–	–	–	19,3	19,00	19,00	350	–	W	3,149	–	–	–
$WB_{0,01}$	0,059	0,9	0,058	–	18,05	17,98	700± 98	–	$W+W_2B$	3,133	5,568	–	–
$WB_{0,02}$	0,118	1,9	0,115	–	18,3	17,95	622± 69	–	$W+W_2B$	3,132	5,600	–	–
$WB_{0,05}$	0,294	4,75	0,290	–	17,86	18,23	640± 76	–	$W+W_2B$	3,130	5,600	–	–
$WB_{0,1}$	0,595	9,91	0,579	–	17,78	17,83	556± 48	–	$W+W_2B$	3,130	5,559	–	–
$WB_{0,2}$	1,156	16,69	1,16	–	16,94	17,20	772± 107	2460± 161	$W+W_2B$	3,130	5,547	–	–
$WB_{0,4}$	2,30	28,6	2,25	–	16,90	17,61	769± 163	2599± 108	$W+W_2B$	3,129	5,562	–	–
$WB_{0,5}$	2,86	33,3	2,86	16,72	16,7	14,71	–	2420± 120	W_2B	–	5,564	–	–
$WB_{0,8}$	4,30	44,4	4,26	–	16,60	14,51	–	2084± 193	$(W_2B)+WB$		5,550	3,124	–
$WB_{1,0}$	5,56	50,0	5,45	16,0	16,70	14,08	–	3752± 176	$(W_2B)+WB$		–	3,131	–
$WB_{1,5}$	8,11	60,0	8,15	–	15,85	15,68	–	3774± 457	$WB+(W_2B_5)$	–	–	3,130	2,980

Calculated composition, WB_x	B, wt. %	B, at. %	Actual B content in alloy, wt. %	Calculated specific gravity	Specific gravity after hot pressing	Specific gravity after annealing	Microhardness, kg/mm², "white phase"	Microhardness, kg/mm², "gray phase"	Phase composition	Lattice periods of phases, Å: W	Lattice periods of phases, Å: W_2B	Lattice periods of phases, Å: WB	Lattice periods of phases, Å: W_2B_5
$WB_{2,0}$	10,52	66,7	10,39	–	15,04	15,00	–	1764±103	$(WB)+W_2B_5$	–	–	3,130	2,974
$WB_{2,5}$	12,80	71,4	12,79	13,1	13,00	11,05	–	2050±200	W_2B_5	–	–	–	2,980
$WB_{3,0}$	13,95	75,0	12,95	–	12,70	11,30	–	2364±196	W_2B_5	–	–	–	2,981
$WB_{4,375}$	20,37	81,4	15,24	–	12,46	11,60	3600±95	2599±120	$B+W_2B_5$	–	–	–	2,983

At a content of 16.69 at. % B in the alloy, its grains occupy up to 40% of the area of the polished section. The white phase, which apparently represents a solid solution of boron in tungsten, has a hardness of 550–770 kg/mm², practically unchanged with the composition of the alloy up to a content of 28.06 at. % B. The hardness of the gray phase, the boride W_2B, is 2420 ± 120 kg/mm². With a further increase in the boron content in the alloys from 33.3 to 50 at. %, the WB phase appears; its hardness rises within these limits of boron concentration from ~ 280 to ~ 3700 kg/mm².

Increasing the boron content to 60 at. % and higher causes the appearance of a phase colored dark gray, with a hardness that increases regularly from 1764 kg/mm² (at 66.7 at. % B) to 2599 kg/mm² (at 81.4 at. % B in the alloy). The maximum hardness of this phase agrees well with the hardness of W_2B_5 ( ). Apparently, this phase has a wide homogeneity range (from 66.7 to 75–77 at. % B), since the WB_2 specimen is single-phase, while a second phase, lighter in color, appears only in the specimen with a content of 75.0 at. % B (15.24 wt. %). This latter has a hardness of 3600 kg/mm², which is close to the hardness of boron ( ).

The data of the metallographic investigation are well confirmed by the results of X-ray analysis. The lattice period of the tungsten powder used in the work was 3.149 Å, which agrees rather closely with the latest literature data ( ). Upon adding 0.9 at. % B to tungsten, the period decreases somewhat (to 3.133 Å), after which it remains practically unchanged up to a boron content of 28.6 at. %. All these alloys are two-phase—the second phase is the boride W_2B with periods $a = 5.564$ Å and $c = 4.739$ Å, which exactly agrees with the data of Kiessling (1). The alloys $WB_{0,8}$ and $WB_{1,0}$ are single-phase, if one does not count the presence, in the X-ray pattern of $WB_{0,8}$, of separate very weak lines of W_2B, and represent the boride WB with periods increasing, for example along the a axis, from 3.124 to 3.131 Å. This boride is also observed in the alloys $WB_{1,5}$ and WB_2, but in the form

a small number of weak lines on the X-ray patterns. Beginning with the composition $WB_{1.5}$, the principal phase is the boride W_2B_5 with a maximum period $a = 2.983$ Å (according to Kiessling, 2.982 Å). In the specimen with 75.0 at. % B, in addition to the W_2B_5 lines, boron lines are observed, identified by comparing interplanar spacings with the use of data $^{(10)}$.

On the basis of the data obtained, the following phase regions of the tungsten —boron system (from 1 to 70-80 at. % B) may be outlined:

1) the α-region of a very limited solid solution of boron in α-W, formed with a decrease in the lattice period and a corresponding distortion, leading to an increase in hardness from 340 to 550-770 kg/mm²;

2) a two-phase region $\alpha + \gamma$, the γ-phase (W_2B) having a very narrow homogeneity range and a hardness of 2420 kg/mm²;

3) a two-phase region $\gamma + \delta$ (W_2B + WB);

4) a homogeneity region of WB (the δ-phase), extending at least from 44.4 to 50-55 at. % B, with hardness varying within these limits from 2080 to 3752 kg/mm²;

5) a two-phase region $\delta + \varepsilon$ (WB + W_2B_5);

6) a homogeneity region of W_2B_5, probably fairly broad—from 68 to 75 at. % B—which does not agree with Kiessling' s earlier data $^{(1)}$ on the absence, or only a very narrow range, of homogeneity of W_2B_5. Evidently, a phase containing less than 71.4 at. % B is formed by the type of subtraction of boron atoms, and one with more than 71.4% by the type of interstitial incorporation.

The comparatively low hardness of the γ-phase (W_2B) is associated with the isolated position of the boron atoms in the unit cell, whereas the δ-phase (WB), with boron atoms linked into zigzag chains, has the maximum hardness. The hardness of the ε-phase (W_2B_5) is somewhat lower than the hardness of the δ-phase, probably as a result of the formation of boron-atom layers that make the alloy more prone to shear deformation, especially since the ε-phase may be regarded as having a simple hexagonal lattice with boron atoms in its interstices.

In addition, the W_2B_5 phase does not possess a high degree of ordering, which is manifested, in particular, in its ability to form wide ranges of solid solutions with other borides as the solvent $^{(11)}$.

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