PHASE EQUILIBRIA IN THE SYSTEM Zr-W-C

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The system Zr-W-C was studied by the methods of X-ray diffraction and microstructural analyses; its phase equilibria determined in as-cast and annealed alloys at 1500 and 1950°C.

This system has frequently attracted the attention of investigators, who, however, restricted themselves to the study of alloys in the section Zr-WC. Thus, Agte and Alterthum first established the absence of a continuous series of solid solutions between ArC and WC [1]. Ya. S. Umanskii carried out an X-ray diffraction examination of alloys in this system and found that, at 2000°C, up to 30 mol.% WC dissolves in ZrC [2]. Nowotny and Kieffer showed that the solubility of WC in ZrC attains 15-20 mol.% at 1600°C and about 35 mol.% at 2100°C; as a result of the dissolution of WC, the lattice constant a of the ZrC alloy decreases from 4.673 to 4.569 A (at 34 mol.% WC) [3]. The microhardness of a homogeneous alloy containing 75 mol.% ZrC and 25 mol.% WC is 3230 daN/mm^2 [4]. In view of the incomplete knowledge of the system Zr-W-C, the present investigation was undertaken with the object of determining phase equilibria in this system and of plotting the corresponding isothermal sections.

BINARY SYSTEMS

System Zr-W. According to the phase diagram given by Hansen and Anderko [5], the compound ZrW$_2$, having a MgCu$_2$-type structure (a = 7.63 or 7.615 A), forms in the system Zr-W at 2150°C in a peritectic reaction. The solubility of tungsten attains 4 at.% in β-Zr at 1660°C and 0.25 at.% in α-Zr at 860°C. At the temperature of peritectic reaction, tungsten dissolves 6 at.% Zr.

System Zr-C. The phase diagram of the system Zr-C is given in [6]; the presence of the compound ZrC, with a homogeneity region between 35 and 50 at.% C at 1400°C and a NaCl-type crystal structure, was established. With increasing carbon content within the homogeneity region, the lattice constant a increases from 4.675 to 4.694 A. The solubility of carbon in α- and β-Zr is very slight.

System W-C. Tungsten forms two carbides, W$_2$C and WC [5]. The carbide W$_2$C forms with a maximum at 2750°C; its homogeneity region extends between 28 and 32 at.% C at 2500°C, and grows narrower at lower temperatures. W$_2$C is known to have several crystalline modifications: The high-temperature modification β-W$_2$C has a NaCl-type structure [7], while α-W$_2$C has a hexagonal Mo$_2$C-type structure (a = 2.994 A, c = 4.724 A, c/a = 1.578 [5]. There are indications of the existence of another W$_2$C modification at 800°C, having a rhombic structure [8]. The carbide WC forms at 2600°C by a peritectic reaction at constant composition. It has a hexagonal WC-type structure (a = 2.906 A, c = 2.837 A, c/a = 0.976) [5].

EXPERIMENTAL STUDY

Specimens for the investigation were made from zirconium (99.84%), tungsten (99.8%), and carbon black (99.5%) powders. After thorough mixing, the starting materials were wetted with a solution of glycerin in methyl alcohol and were then compacted. Sintering was performed for 30 min at 1500°C in a retort furnace with a graphite heating element in a vacuum (10^{-3} mm Hg) or in a TVV-2 furnace. All the specimens were then remelted in an arc furnace with a nonconsumable tungsten electrode on a water-cooled copper hearth, in a helium atmosphere at a pressure of 300-400 mm Hg.

Both as-cast and annealed alloys were investigated. The specimens were annealed in a TVV-2 furnace for 120 h at 1500°C, in a stream of pure argon. Some of the specimens (mainly those of alloys from the ZrC-WC section)
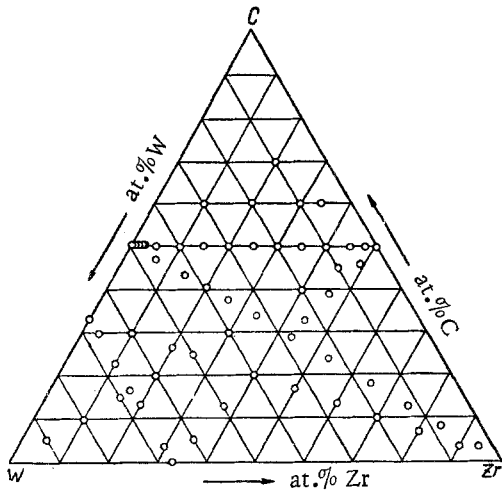
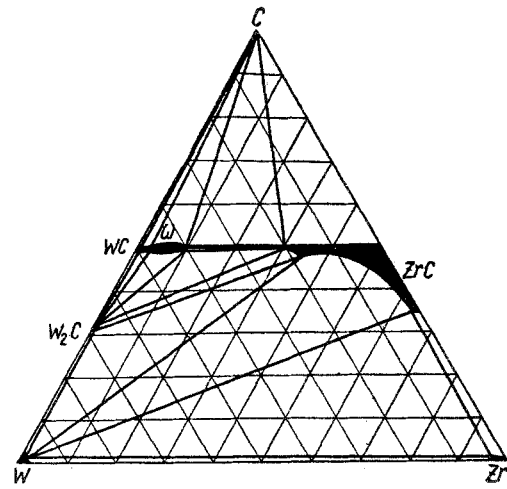Fig. 1. Compositions of Zr-W-C alloys investigated.
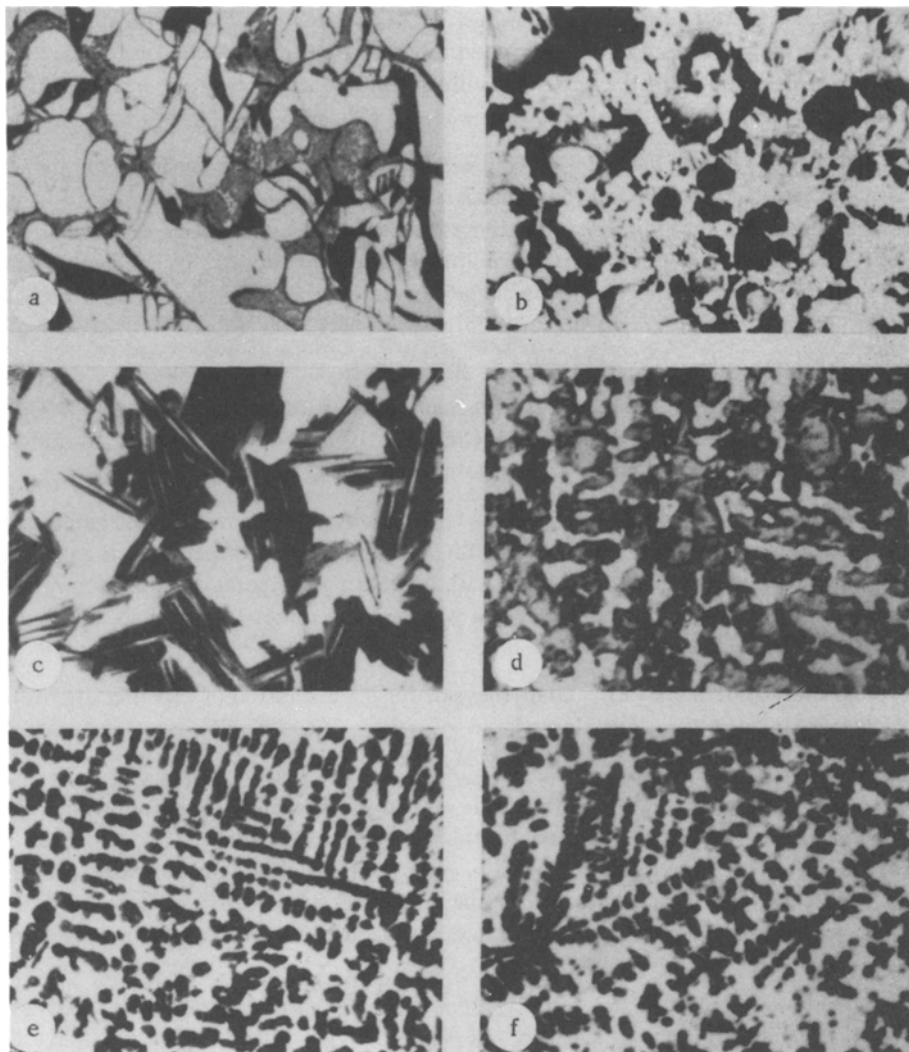

Fig. 2. Phase equilibria in as-cast Zr-W-C alloys.

Fig. 3. Photomicrographs of alloys: a) 10 at.% Zr, 80 at.% W, 10 at.% C. ×340; b) 40 at.% Zr, 20 at.% W, 40 at.% C. ×200; c) 10 at.% Zr, 67 at.% W, 23 at.% C. ×200; d) 54 at. % Zr, 23 at.% W, 23 at.% C. ×450; e) 34 at.% Zr, 33 at.% W, 33 at.% Cr; f) 20 at.% Zr, 40 at.% W, 40 at.% Cr. ×340.

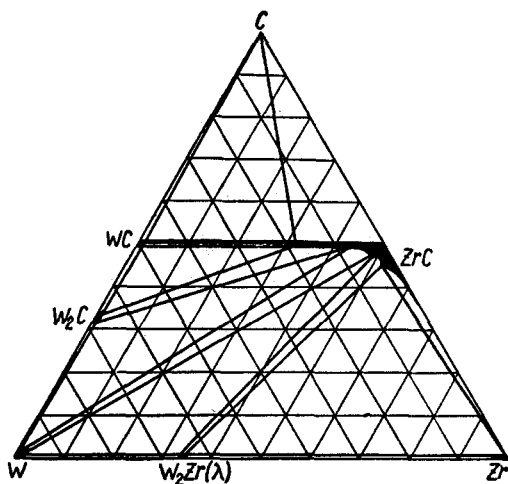Fig. 4. Isothermal section of system Zr-W-C at 1500°C.

were also annealed for 80 h at 1950°C. All alloys were examined by the X-ray diffraction and microstructural methods. The X-ray diffraction study was made by the powder method in chromium radiation in cameras of 57.3-mm diameter. A 1:1 mixture of concentrated HF and HNO_3 was the etching reagent in the microstructural study.

The composition of 60 alloys in the system Zr-W-C are shown in Fig. 1. The study of as-cast alloys (Fig. 2) demonstrated that the ZrC-base solid solution containing about 40 mol. % WC is in equilibrium not only with α-Zr, W, and W_2C, but also with a new phase, termed the ω-phase. The homogeneity region of the ω-phase extends along the 50 at.% C line at 2-10 at.% Zr. Diffraction pictures of the ω-phase indicate a cubic system corresponding to a NaCl-type crystalline structure. The lattice constant a of the ω-phase increase from 4.25 ± 0.01 to 4.30 ± 0.01 A as zirconium content increases from 2 to 10 at.%. Alloys containing 15-30 at.% Zr + 50 at.% C consist of two phases—ω +(Zr, W) C. Interference lines in the diffraction picture of these alloys are very diffuse, and form whole bands, which may indicate that, as in the case of the system ZrC-MoC [2], a wider region of the solid solution of WC in ZrC attaining 96 mol.% exists near the melting point. Even when the alloys are cooled rapidly, this solid solution undergoes decomposition with the formation of the (Zr, W)C solid solution and the isostructural ω-phase. Figure 3 shows photomicrographs of some as-cast alloys: a, b) (Zr, W)C + W; c) (Zr, W)C + W_2C.

Phase equilibria in the alloys annealed at 1500°C are shown in Fig. 4. The lattice constant values found for the W_2C, WC, and ZrW_2 phases in the two- and three-phase alloys coincide with those reported in the literature. This indicates the absence of the solubility of zirconium in tungsten carbides and of carbon in the compound ZrW_2. The carbide ZrC dissolves 34 mol.% WC, the value of the constant on the boundary of this solid solution being a = 4.57 A. The phase diagram was plotted from measured values of the lattice constant of the solid solution (Zr, W)W in the two- and three-phase alloys. The photomicrographs show the following equilibria: (Zr, W)C + ZrW_2 + α-Zr (Fig. 3d), (Zr, W)C + W (Fig. 3e), and (Zr, W)C + W_2C (Fig. 3f).

A study of alloys from the section ZrC-WC was also made on specimens annealed at 1950°C. The lattice constant of the solid solution (Zr, W)C with the maximum WC content is a = 4.55 A. Bearing in mind that the constant a changes linearly with composition, it is found that the solubility of WC in ZrC is 40 mol.%.

This study has shown that the system Zr-W-C is similar to the system Ti-W-C investigated earlier [9]. In both systems, ternary phases are absent; the carbides ZrC and TiC are both characterized by a high solubility of tungsten carbide. The solubility of WC in ZrC rapidly decreases with decreasing temperature, which may be attributed to the difference in the relative sizes of Zr and Ti atoms (Ti and W atoms are closer in size than are Zr and W atoms: r_{Ti} = 1.46 A, r_W = 1.40 A, and r_{Zr} = 1.60 A).

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SUMMARY

The system Zr-W-C was investigated by the methods of X-ray diffraction and microstructural analyses. Phase equilibria at 1500°C were determined for as-cast and annealed alloys. The carbide ZrC dissolves 34 mol.% WC at 1500°C; at 1950°C, the solubility of WC increases to 40 mol.%. As-cast alloys contain the ω-phase, which has a cubic NaCl-type structure (a = 4.25-4.30 A), and is distributed along the 50 at.% C line at 2-10 at.% Zr. It is shown that the solubility of WC in ZrC may be even greater at temperature approaching the melting point of the alloys.

LITERATURE CITED

1. C. Agte and H. Alterthum, Z. techn. Physik, 11, 182 (1930).
2. Ya. S. Umanskii, Izv. Sektora Fiz.-Khim. Anal., 16, 127 (1943).
3. H. Nowotny and R. Kieffer, Metallforschung, 2, 257 (1947).

4. A. E. Koval'skii and L. A. Kanova, Zavodsk, Lab., 16, 1362 (1950).

5. M. Hansen and K. Anderko, Structures of Binary Alloys [Russian translation], Moscow, Metallurgizdat, 1, 2 (1962).

6. F. Benesovskii and E. Rudy, Planseeberiche Pulvermet, 8, 66 (1960).

7. H. J. Goldschmidt and J. A. Brand, Birmingham Small Arms Group Res. Center, 34 (1962).

8. Yu. B. Kuz'ma, V. I. Lakh, V. Ya. Markiv, B. I. Stadnyk, and E. I. Gladyshevskii, Poroshkovaya Met., 4, 40 (1963).

9. H. Nowotny, E. Parthe, R. Kieffer, and F. Benesovskii, Z. Metallkunde, 45, 97 (1954).

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