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INVESTIGATION OF THE OXIDATION RESISTANCE OF ZIRCONIUM
BORIDE-MOLYBDENUM DISILICIDE ALLOYS

Translation

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Abstract

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This translation was prepared from an article originally published as follows: Kuzenkova, M. A., and P. S. Kislyy. Issledovaniye okalinostoykosti splavov borida tsirkoniya s disilitsidom molibdena. IN: Akademiya nauk UkrSSR. Poroshkovaya metallurgiya, no. 10, 1965, 75-79. This work examines the oxidation resistance of pure zirconium boride and zirconium boride-molybdenum disilicide alloys. It was found that the oxidation resistance of the zirconium boride-molybdenum disilicide alloys considerably exceeds that of pure zirconium boride, which, like all the other borides of transition metals, begins to oxidize in an oxygen or air medium at temperatures of only 700-800°C. The authors cite an article written earlier by them which describes how these alloys were obtained. The present article describes the process by which they oxidize the specimens. The zirconium boride specimens do not disintegrate, however, because it was found that they are covered with a protective film. Protective films are also formed in the oxidation process of the zirconium boride-molybdenum disilicide alloys, this process differing from that of pure zirconium boride. The films are analyzed and their effect is discussed. The authors explain the reason for the higher protective properties of the films formed on the alloys as compared to those formed on pure zirconium boride and they conclude that the zirconium boride-molybdenum disilicide alloys possess an exceptionally high oxidation resistance and can be used at temperatures up to 1500-1550°C. The original article included 5 references.

FOREWORD

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INVESTIGATION OF THE OXIDATION RESISTANCE OF ZIRCONIUM BORIDE-MOLYBDENUM DISILICIDE ALLOYS

Work [1] describes how zirconium boride-molybdenum disilicide alloys are obtained and gives some of their physical properties. The oxidation resistance of these alloys considerably exceeds that of pure zirconium boride, which, like all the other borides of transition metals, begins to oxidize in an oxygen or air medium at temperatures of only 700—800°C. The friable and fragile oxides which are formed on borides at low temperatures crumble from the surface of the specimens and do not protect them against further disintegration [2].

To raise the oxidation resistance, it was proposed to alloy the borides with silicon and silicides [3—6]. The oxidation resistance of binary borides $(\text{Ti}, \text{Cr})\text{B}_2$ with added silicon and molybdenum disilicide at temperatures of 1000 to 1200°C was investigated in works [4] and [5], and it was demonstrated that the resistance considerably exceeds that of pure borides.

This work examines the oxidation resistance of pure zirconium boride and zirconium boride-molybdenum disilicide alloys. Work [1] describes how these alloys were obtained. Cylindrical specimens, 8 mm in diameter and 12 mm long, produced by hot pressing and rod shaped specimens, 8 mm in diameter and 200 mm long, produced by hot extrusion of plasticized powder mixtures followed by sintering were subjected to oxidation. The porosity of hot-compacted zirconium boride specimens amounted to ~ 8%, while that of the extrusion specimens is given in table:

Alloy	ZrB_2	$(\text{ZrB}_{1,9})_{23} \cdot \text{MoSi}_{1,1}$	$(\text{ZrB}_{1,7})_{13} \cdot \text{MoSi}_{1,2}$	$(\text{ZrB}_{1,6}) \cdot \text{MoSi}_{1,4}$	$\text{ZrB}_2 + 20\% \text{MoSi}_2$	$\text{ZrB}_2 + 25\% \text{MoSi}_2$
					(as charged)	
Porosity of rods, in %.	~15	5—7	5—9	9—13	10—15	35

Resistance heating was used to oxidize the rods in the air. The desired temperature of the specimens was reached by continuously adjusting the voltage by means of an autotransformer, the temperature being measured by the optical micro-pyrometer OMP-043. The oxidation rate was determined by the variation of the mass per surface unit of a 20—30-mm long central section of the rod where no temperature drop was observed during heating, as well as by the thickness of the corrosion layer measured by a microscope.

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Alloy	ZrB ₂	(ZrB _{1,9}) ₂₃ · ·MoSi _{1,1}	(ZrB _{1,7}) ₁₃ · ·MoSi _{1,2}	(ZrB _{1,6}) ₈ · ·MoSi _{1,4}	ZrB ₂ + +20% MoSi ₂	ZrB ₂ + +25% MoSi ₂
	(as charged)					
Porosity of rods, in %.	~15	5—7	5—9	9—13	10—15	35

Resistance heating was used to oxidize the rods in the air. The desired temperature of the specimens was reached by continuously adjusting the voltage by means of an autotransformer, the temperature being measured by the optical micro-pyrometer OMP-043. The oxidation rate was determined by the variation of the mass per surface unit of a 20—30-mm long central section of the rod where no temperature drop was observed during heating, as well as by the thickness of the corrosion layer measured by a microscope.

The hot pressed specimens were oxidized in a tubular furnace equipped with Silit heaters. The oxidation resistance was determined by the variation in the mass per surface unit. Generally, this is not a rigid value by which the amount of the oxidized zirconium boride may be judged because the friable films which are formed at oxidation temperatures up to 1000—1100°C crumble and, obviously, partly evaporate.

Kinetic oxidation curves for specimens made of pure zirconium boride are given in Fig. 1, which shows that at temperatures of 800—1000°C (1, 2 and 3), the mass variation increases linearly with the oxidation time, i.e., no delaying processes obstruct the passage of oxygen to the surface of

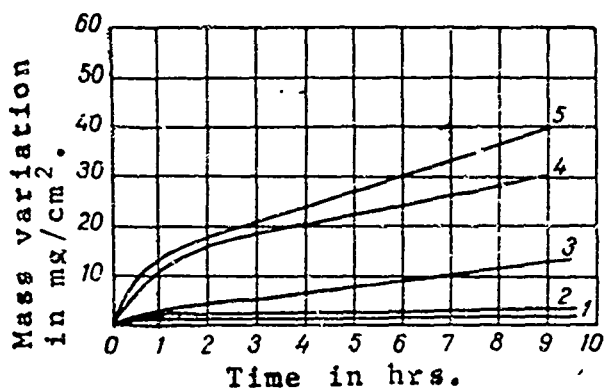


Fig. 1. Kinetic oxidation curves for pure zirconium boride with porosities of 8% (1 and 2) and 15% (3, 4, and 5), at various temperatures, in °C

1 - 800, 2 - 1000, 3 - 1000, 4 - 1200, and 5 - 1400.

the specimen. The oxidation intensity is considerably higher for porous specimens (3). In addition, specimens with about a 15% porosity practically completely disintegrate within 8—10 hrs after oxidation even though the mass increase seems to be insignificant.

The variation in the mass of specimens oxidized at temperatures of 1200 and 1400°C (4 and 5) is considerably greater. However, they do not disintegrate, because it was found that they are covered with a protective film. The shapes of the oxidation curves show that, in this case, the specimens are oxidized intensely within the first 2—3 hrs, and become covered with a protective film preventing free penetration of the oxygen into the base material. In addition, after a 2-hr oxidation, the relationships are linear and, for temperatures of 1200 and 1400°C, they are expressed

by the equations:

$$\frac{\Delta P}{S} = 1,8\tau + 13; \quad \frac{\Delta P}{S} = 3\tau + 11,5, \text{ respectively.}$$

The formation of the glasslike boric anhydride which, combining with zirconium oxide, turns into the corresponding borates [2] and [7], accounts for the development of a dense oxide film at temperatures above 1200°C. The glasslike nature of the developed film prevents oxygen diffusion to a great degree but does not stop it. This film disintegrates at 1450°C. Obviously, when the glasslike borates are at this temperature, a portion of plane triangular BO₃ groups are transformed to tetrahedral EO₄ complexes [8], resulting in the blistering of the film and local damage to the specimen.

The oxidation process of the zirconium boride-molybdenum disilicide alloys differs from that of pure zirconium boride. As seen from Fig. 2, which presents kinetic oxidation curves for zirconium boride-molybdenum disilicide alloys, (ZrB_{1.9})₂₃MoSi_{1.1} and (Zr_{1.7})₁₃MoSi_{1.2}, the latter as well as

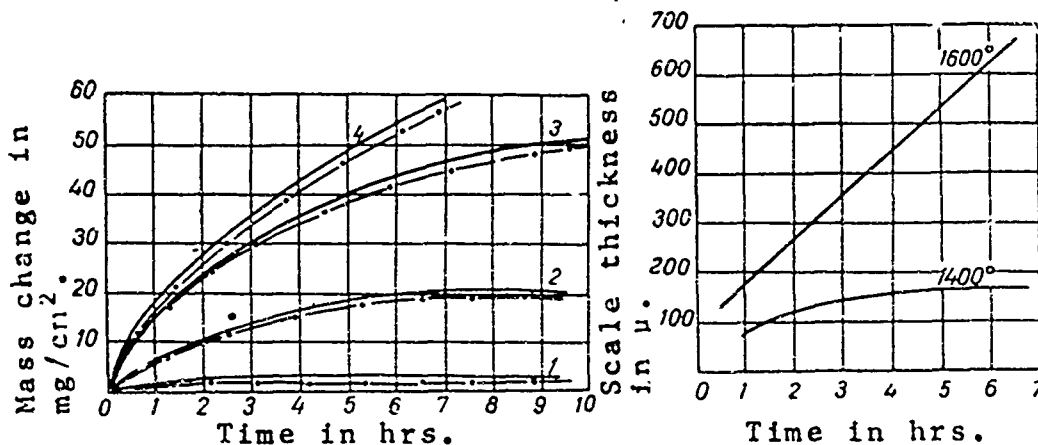


Fig. 2. Kinetic oxidation curves for zirconium boride-molybdenum disilicide alloys at various temperatures in °C

Fig. 3. Dependence of (ZrB_{1.9})₂₃MoSi_{1.1} alloy on the oxidation time at various temperatures.

1 - 1000, 2 - 1400, 3 - 1500, and 4 - 1600.
Solid lines: (ZrB_{1.9})₂₃MoSi_{1.1}.
Dash-dot lines:
(Zr_{1.7})₁₃MoSi_{1.2}.

pure zirconium boride exhibit a linear dependence of the mass variation of the specimen on the exposure period at 1000°C, and this indicates free access of oxygen to the specimen.

At high temperatures (up to 1500—1550°C), this dependence takes on a parabolic character, i.e., up to these temperatures, the films which are formed are protective, and they hinder the process of oxygen transfer to the alloy. In the region where the parabolic law is satisfied, the constant of the oxidation rate of the alloys is 67.1 and 300 mg/cm² x hr, for 1450 and 1500°, respectively, which indicates their high scale resistance. At 1600°, there is an almost linear variation in weight with time. The linear character of the oxidation of the alloys at 1600° is seen particularly clearly when observing the variation in the thickness of oxide film (Fig. 3); at 1400°, the relationship is of a parabolic character.

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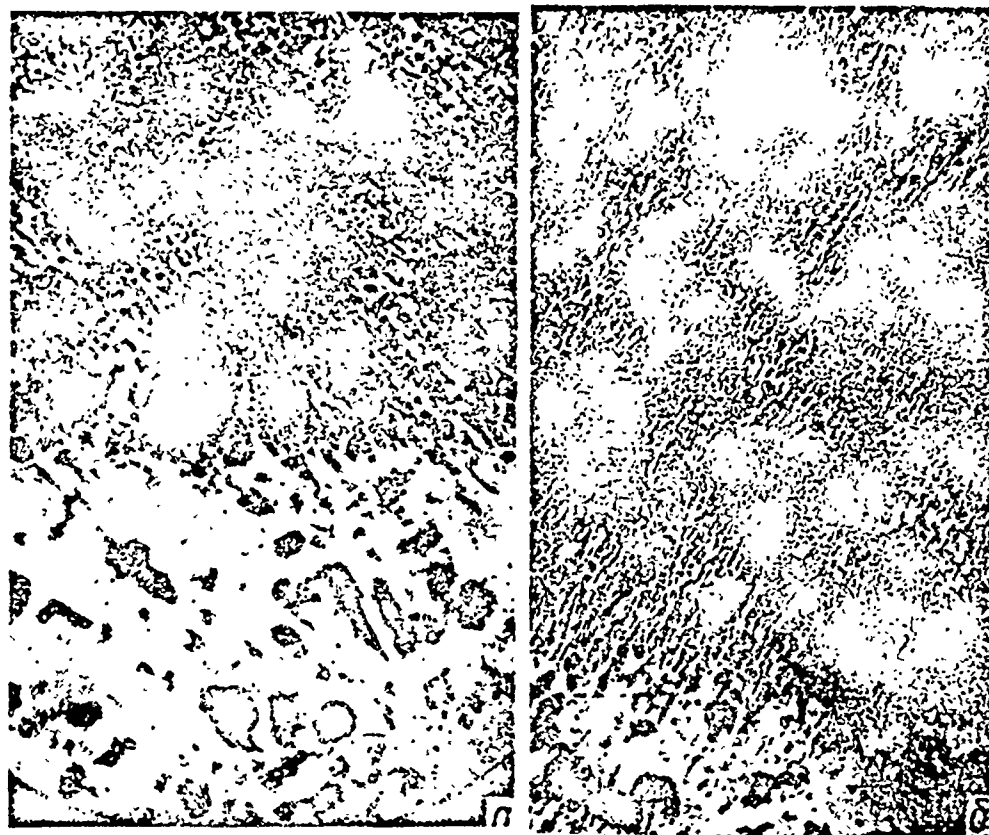


Fig. 4. Microphotos of the oxide films on the $(ZrB_{1.9})_{23}MoSi_{1.7}$ alloy oxidized at 1400°C (left), and 1500°C (right) x 500.

I - Base material; II - film.

A microstructural analysis indicated that films, obtained within a temperature range where the parabolic law of oxidation is satisfied, are continuous, contain some closed