OXIDATION RESISTANCE OF (Zr, Hf)B_2 SOLID SOLUTION

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The oxidation resistance of the ZrB_2-HfB_2 solid solutions in the temperature range of 1500-1600°C was carried out. The solid solutions have a higher oxidation resistance than individual phases due to the thin oxide layer. The highest oxidation was observed in solid solutions close to HfB_2, due to the formation oxide phases with a low diffusion rate of oxygen into the material. The main oxidation mechanism is the reaction of a diboride-based solid solution with oxygen and the formation of an oxide-based solid solutions with saving the Zr/Hf ratio.

Keywords: oxidation, zirconium diboride, hafnium diboride, solid solutions

Introduction. The necessity to develop the high-temperature materials that can operate in an oxidizing environment at temperatures above 1500 °C requires to create high-temperature ceramic materials based on group IV-VI transition metal diborides, because they have high oxidation resistance [1–3], melting temperature [4], thermal conductivity [5, 6] and heat resistance [7, 8].

At the same time, the rapid development of multicomponent materials, in particular ceramics, shows that solid solutions have better properties than individual components [9]. Among all diborides we can emphasized only ZrB_2 and HfB_2 because they have highest properties at high temperature [10–13]. The different solid solutions were obtained in [14–17]. However, there are no results on high-temperature properties, in particular, oxidation resistance at high-temperature above 1500 °C. Therefore, the purpose of the present study is investigating the oxidation resistance and oxidation mechanisms of solid solutions based on ZrB_2-HfB_2.

Materials and methods. The commercially available powders were used in this work: ZrB_2 (d=1–2 μm, O: 0.5 wt. %), HfB_2 (d=3–4 μm, O: 0.8 wt. %). The amount of hafnium diboride in (ZrB_2-HfB_2) powder mixture was 25, 50 and 75 at.%. The powder mixture was mixed in a SAND-1 planetary milling from 5 hour with acetone milling medium.

Hot pressing was carried out at a temperature of 2100 °C, pressure of 32 MPa with holding time of 30 minutes. The microstructure of the as-sintered ceramics was studied using the scanning electron microscopy Tescan Mira 3 device (Czech Republic), with X-ray spectral analysis (EDS) by Oxford X-Max sensor (UK).

High-temperature oxidation test was carried out on samples polished from all sides with dimensions of 3.5 mm x 4.5 mm x 20 mm, which were placed on point supports made of zirconium oxide in an LHT 01/17 D furnace

(Nabertherm, Germany). The oxidation test did in laboratory air at 1500-1600°C with exposure for 2 hours. The heating rate was 6 °C/min, cooling took place together with the furnace.

Results and discussion. The microstructure of hot-pressed materials was heterogeneous. The main phase were ZrB_2, HfB_2, solid solutions $(Zr_x,Hf_y)B_2$ and porosity. It should be noted that single phase ZrB_2 and HfB_2 have high residual porosity, Table 1. At the same time addition of ZrB_2 to HfB_2 or vice versa leads to an increase density due to the activation of the grain boundary and volume boundary diffusion. The ratio between the phases in the microstructure depends on the ratio between ZrB_2 and HfB_2 in the powder mixture, Table 1.

The chemical composition of the solid solution for materials containing HfB_2 in the amount of 25, 50, 75 mol. % was $(Zr_{0.75}Hf_{0.25})B_2$, $(Zr_{0.5}Hf_{0.5})B_2$, and $(Zr_{0.25}Hf_{0.75})B_2$, respectively. The inclusion of pure ZrB_2 and HfB_2 was also observed in the microstructure, the ratio between which is given in Table 1.

Table 1. Material, phase composition, Thickness of oxide scale $(Zr,Hf)B_2$ solid solution

Material	Phase composition, vol. %				Thickness of oxide scale, μm	
	ZrB_2	ss*	HfB_2	Porosity	T-1500°C	T-1600°C
ZrB_2	86	-	-	14	328.1±4.3	579.9±31.2
ZrB_2-25 % mol. HfB_2	16	74	2	8	186.3±7.6	445.5±18.9
ZrB_2-50 % mol. HfB_2	1.2	89.5	1.5	7.5	88.3±8.0	343.4±17.8
ZrB_2-75 % mol. HfB_2	2	48.7	43.2	6.1	77.8±2.7	289.5±9.8
HfB_2	90	-	-	10	207.3±5.9	358.2±10.9

ss*-solid solution

The cross section of the oxidized ceramic at temperatures of 1500 and 1600°C is shown in Fig. 1. According to the microstructure, oxide scale consists of several oxide layers. The upper layer is an amorphous phase based on B_2O_3 with inclusions of oxides. The bottom part is a layer based on oxide with inclusions of B_2O_3 phase. As we can see the thickness of the B_2O_3 layer was thin (up to 5 μm) at 1600°C, due to an active evaporation from the surface [18].

The layer based on oxides has a hetero genius microstructure, Fig. 1 k-o. Phase composition was ZrO_2, HfO_2 and an oxide solid solution. The process of solid solution of boride solid solution can be described by the following reaction equations:

$$ZrB_2+2.5O_{2(g)}=ZrO_2+B_2O_3 \quad (1)$$

$$HfB_2+2.5O_{2(g)}=HfO_2+B_2O_3 \quad (2)$$

$$(Zr_xHf_y)B_2+2.5O_{2(g)}=(Zr_xHf_y)O_2+B_2O_3 \quad (3)$$

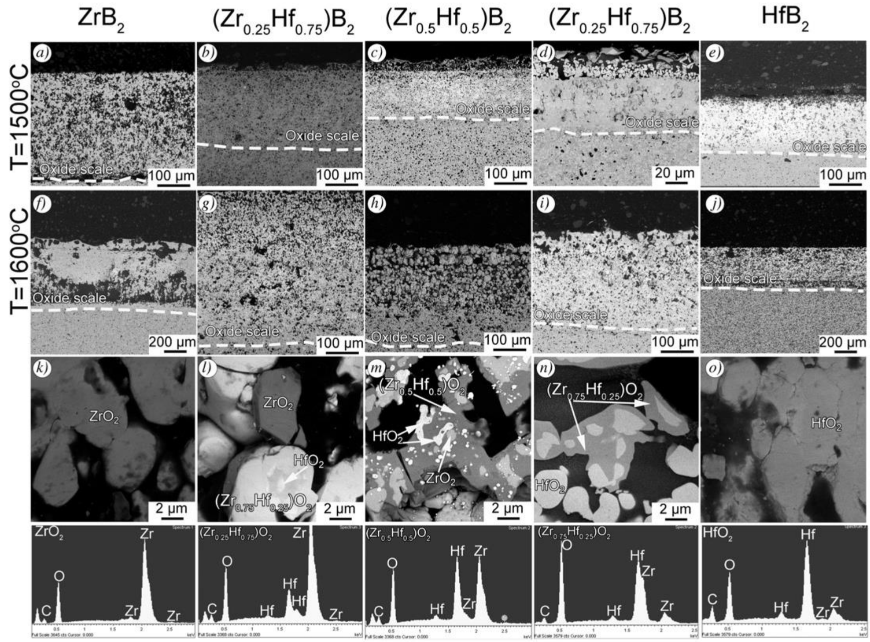

Fig. 1 Preliminary section of solid solution (Zrx,Hfy)B2 after oxidation at temperatures of 1500°C (a-e) and 1600°C (f-j).

Solid solutions based on diborides had the different mechanism of oxidation than pure ZrB_2 or HfB_2. The ratio between the metals in the oxide and diboride solid solution was the same, which indicates the high stability of diboride phase, Fig.1. It means that diboride solid solutions do not decompose into separate phases during oxidation. It should emphasize that an increase in the amount of hafnium oxide in solid solution leads to an increase in the phase transition temperature [19]. This makes the formed scale completely stable at temperatures of 1500-1600°C.

Therefore, solid solutions had higher oxidation resistance than pure diborides due to the formation of denser oxide scale on the surface. High oxidation resistance was observed for the $(Zr_{0.25}Hf_{0.75})B_2$ composition due to the formation of dense $(Zr_{0.25}Hf_{0.75})O_2$ oxide phase which reduce the diffusion of oxygen into the material due to the higher activation energy of oxygen diffusion [20].

Conclusions. The introduction of HfB_2 into ZrB_2 leads to an increase density of ceramics and the formation of solid solutions. The chemical composition of the solid solution depends on the content of HfB_2 in slid solution. The oxidation resistance of solid solutions is higher than individual diborides.

The maximum oxidation resistance was observed in solid solutions close to hafnium diboride.

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