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Effect of chromium additive on sintering and oxidation behavior of HfB_2-SiC ceramics

D. Bannykh[a,b], A. Utkin[a,*], N. Baklanova[a]

[a] Institute of Solid State Chemistry and Mechanochemistry SB RAS, 18 Kutateladze st., Novosibirsk 630128, Russia
[b] Novosibirsk State University, 1 Pirogova st., Novosibirsk 630090, Russia

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ABSTRACT

The effect of chromium admixture on the processes in the HfB_2-SiC ceramic powder system during its pressureless sintering at 1600 °C was studied. It was shown that an increase in chromium content from 0% to 15.5% in the HfB_2-SiC ceramic powder mixture leads to a continuous increase in its relative density up to 90%. A transient liquid phase Cr-Si-C-B is formed at 1600 °C, and it promotes intense sintering of HfB_2 and SiC powders. The oxidation resistance of HfB_2-SiC-Cr ceramics was studied in static air at 1000–1500 °C. It was shown that the oxidation resistance is greatly improved due to a decrease in the porosity of the sintered ceramic system because of chromium additive. The presence of chromium oxide in the formed surface glassy layer can also lead to the increase in the oxidation resistance. These results suggest that chromium can be considered as a promising sintering additive for HfB_2-SiC and similar systems.

1. Introduction

Transition metal borides, carbides, and nitrides are gaining increased attention as refractory compounds with superior properties at very high temperatures. Hafnium and zirconium diborides, especially combined with ~20 vol% of silicon carbide, display a number of unique properties such as hardness, high thermal conductivity, thermal and chemical stability [1]. It was stated that the structural stability and thermal conductivity of diboride-based ceramics are higher than those of carbides and nitrides [2]. The same is true for flexural strength and fracture toughness [3]. These kinds of ceramics are also able to retain their strength up to high temperatures in air. It was well documented that silicon carbide greatly improves the oxidation resistance of HfB_2 and ZrB_2 due to the formation of a protective glass layer composed of SiO_2/B_2O_3 during oxidation [4].

Due to the high melting points of HfB_2 and ZrB_2 (3380 and 3245 °C, respectively), the fabrication of dense and durable HfB_2 or ZrB_2-based ceramics requires special high-temperature sintering techniques, e.g. hot pressing (HP) or spark plasma sintering (SPS). A typical sintering temperature for ZrB_2 – 20 vol% SiC ceramics to achieve a relative density of 98% or higher is about 2000–2200 °C for HP and 1900–2000 °C for SPS [5]. An additional sintering approach is pressureless sintering, which is simpler and more scalable than HP or SPS. However, in order to attain the acceptable density of the MB_2-SiC (M = Hf, Zr) ceramics by pressureless technique, it is necessary to sinter the powder mixtures at very high temperatures. Two common approaches are developed to diminish the sintering temperatures of MB_2-SiC (M = Hf, Zr) powder mixtures, namely, (i) the use of the small-sized initial powders and (ii) sintering additives. The role of the latter has been reported to be dual. On the one hand, the additives promote better sinterability of ceramic particles through different mechanisms, e.g. the removal of oxide impurities that are present on grain boundaries [6]. On the other hand, they can form high-melting complex silica-based oxides with very high oxidation resistance. Several positive examples to sinter the ZrB_2 (HfB_2) and SiC powder mixtures have been reported by several research teams. A few works recently reported the use of tungsten carbide [6], vanadium carbide [7], molybdenum [8], C/B_4C [9] and boron [10] as sintering aids for the ZrB_2-SiC system, as well as tungsten carbide [11] for the HfB_2-SiC system. One can note that the lowest reported temperature of pressureless sintering of such systems was approximately 2000 °C.

An alternative approach to compact the ceramic powders is based on the formation of transient liquid phase (TLP) during the thermal treatment of ceramic powders with some aids [12]. This approach was successfully applied to sinter different kinds of ceramic powders [13,14]. As to the HfB_2-SiC system, it is known that silicon carbide reacts with chromium at 1600 °C and higher with the formation of liquid Cr-Si-C eutectics [15]. One can propose that the transient liquid phase could promote sintering of HfB_2-SiC ceramics at temperatures lower than 2000 °C. Another benefit to use chromium as a sintering

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[*] Corresponding author.
E-mail address: utkin@solid.nsc.ru (A. Utkin).

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Table 1
The composition of the initial powder mixtures.

No.	HfB_2:SiC volume ratio	Cr: SiC molar ratio	ω(HfB_2), wt%	ω(SiC), wt%	ω(Cr), wt%
1	80:20	0: 1	92.9	7.1	0
2		0.5: 1	88.8	6.8	4.4
3		1: 1	85.1	6.5	8.4
4		1.5: 1	81.6	6.2	12.2
5		2: 1	78.5	6.0	15.5

additive is in the fact that the oxidation of the HfB_2-SiC-Cr system at high temperatures could lead to the formation of a protective layer due to the formation of the HfO_2-Cr_2O_3 eutectics (T = 1920 °C) if such ceramic material would be used at temperatures higher than 1900 °C. [16]. Thus, the present work aims to study the effect of chromium additive on the densification behavior, chemical transformations and oxidation resistance of the HfB_2 – 20 vol% SiC ceramics.

2. Experimental

2.1. Synthesis & oxidation

Hafnium diboride (IPK Umeks, 99.5%, Russia), silicon carbide (Volzhsky Abrasive Plant, 99.0%, Russia) and chromium (Rusredmet, 99.0%, Russia) powders were used as starting materials. The volume HfB_2:SiC ratio was constant for all powder mixtures and equal to 80:20%. Chromium content was varied to obtain Cr: SiC molar ratios of 0:1; 0.5:1; 1:1; 1.5:1; 2:1 (Table 1). Powders were mixed and then ground using the AGO-2 high-energy ball mill (Novic Inc., Russia) under acceleration of 40 g for 5–6 min. The balls and the jar were made of hardened stainless steel.

After mixing, the powders were compacted into cylindrical tablets 20 mm in diameter by uniaxial pressing at 200 MPa in a stainless steel die at ambient temperature. The compacts were placed in a high-vacuum high-temperature furnace (SNVE-1.3.1/20, Prizma, Russia) and heated to 1600 °C at a rate of 10 °C/min, kept at this temperature for 2 h, and then cooled at a rate of 5 °C/min.

The relative density and shrinkage of specimens as tablets were calculated from the linear dimensions of tablets measured before and after thermal treatment with 0.1 mm accuracy.

High-temperature oxidation tests were performed at a temperature of 1000, 1250 and 1500 °C in static air. The compacts of different composition were placed in the furnace (PVK-1,6-5, Teplopribor, Russia), heated to the required temperature (1000, 1250 or 1500 °C), kept for 60 min at this temperature, and cooled in the furnace to the ambient temperature. The measurements of the masses of the samples before and after oxidation were carried out with an accuracy of 0.1 mg.

2.2. Characterization

Sample morphology and the local elemental compositions were studied with high-resolution scanning electron microscopes MIRA 3 LMU, (TESCAN, Czech Republic), as well as TM-1000 (Hitachi, Japan), coupled with energy dispersive X-ray spectroscopy (EDX) instruments INCA Energy 450 XMax 80 and Swifted-TM, respectively. To determine the elemental composition, the compacts under investigation were packed with epoxy, cross-sectioned and polished using Tegramin-30 (Struers) polishing machine with the 1 μm diamond suspension (MonoSyn Duo, Synercon, Germany), and then coated with a conductive carbon layer.

X-ray diffraction (XRD) patterns of the powders and compacts were recorded with a D8 Advance (Bruker, Germany) powder diffractometer using Cu-K_α (λ_1 = 1.54056 Å, λ_2 = 1.54439 Å) radiation, equipped with a one-dimensional Lynx-Eye detector and K_β filter. XRD patterns were collected in the interval $30^\circ < 2\theta < 130^\circ$. Quantitative and qualitative analysis of XRD powder patterns was performed by the Rietveld method using Topas 4.2 (Bruker) and Search-Match (Oxford Cryosystems) software, respectively. The PDF-4 + (ICDD, USA) and ICSD (FIZ Karlsruhe, Germany) databases were used.

3. Results and discussion

3.1. SEM/EDX analysis of the powders

The morphology of powder mixtures before and after grinding was examined by SEM analysis. The grain sizes of as-received HfB_2, SiC and Cr were approximately 150, 200 and 50 μm, respectively. According to SEM data, after milling the HfB_2 and Cr grain sizes decreased to 1–2 μm while SiC powder was ground just to 2–7 μm fraction, which can be explained by the very high hardness of SiC. With an increase in milling time to 10–20 min, SiC grain size was found to reduce to 2–3 μm. However, rather large amount of iron (more than 3 wt%) was detected in the target product. The iron impurity originates from the wear of steel grinding media. So, grinding time was chosen to be 5–6 min, which allowed us to obtain close-to-homogeneous powder mixtures with 1–7 μm grains. According to EDX data, the compositions of ground powder mixtures corresponded to the initial ones, and iron content was less than 1.5 wt%.

It is noteworthy that no iron compounds were detected in the products by XRD analysis. Therefore, it could be proposed that iron appears to be dissolved in chromium compounds. The XRD patterns indicated that no new phases were formed during high-energy milling. Thus, the compositions of ground powder mixtures corresponded to the initial ones and included HfB_2, α-SiC, and Cr.

3.2. Sample density

The relative density of the samples sintered at 1600 °C for 1 h was measured as a function of chromium content (Fig. 1). One can note that the relative density of chromium-free compacts was ~ 64%, which is rather low and close to that of unheated compacts (~ 60%). This result is in good agreement with data reported in [11] that intense pressureless sintering of HfB_2-SiC powder mixtures starts at a temperature as high as 2000 °C.

It should be stressed that chromium-containing samples exhibited the isotropic shrinkage of tablets. The sizes of the obtained tablets decreased monotonously with an increase in chromium content; no shape distortion was observed. One can see in Fig. 1 that the density of sintered powder mixtures containing chromium is higher, and it increases continuously up to ~ 90% as the chromium content in the mixture increases to 15.5%. Thus, it can be suggested that chromium promotes

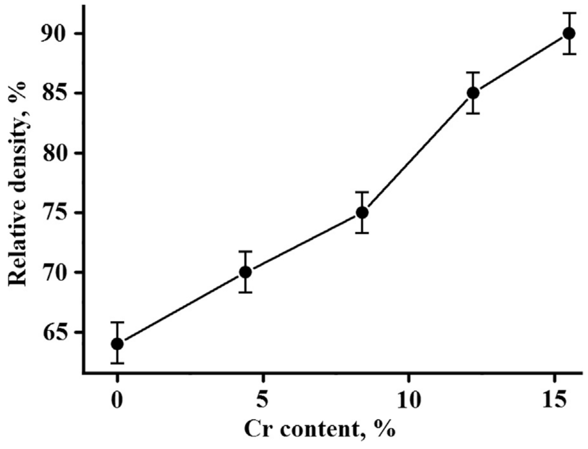

Fig. 1. The relative density of sintered samples depending on chromium content.