

Mechanical properties and oxidation resistance of ZrB₂-SiC-MoSi₂ ceramic prepared by spark plasma sintering

Qi Li^{1*}, Lamei Cao¹

¹Science and Technology on Advanced High Temperature Structural Materials Laboratory, Beijing Institute of Aeronautical Materials, Beijing 100095, China

*Corresponding author e-mail: liqi1988china@126.com

Abstract. ZrB₂-30vol.%SiC-10vol.%MoSi₂ ceramic with high relative density were fabricated by spark plasma sintering method (SPS). The comprehensive performances, including microstructure, mechanical properties, oxidation resistance, were evaluated. MoB phase was formed during sintering, therefore, the interphase bonding forces among different phases were significantly enhanced. The fracture toughness, hardness and bending strength were 5.73 MPa·m^{1/2}, 16.1 GPa and 428 MPa, respectively. By oxidation at 1500 °C for 10 h, the mass gain was about 14.42 mg/cm², the oxidation depth was about 298 μm.

1. Introduction

Recent years, hypersonic aircraft have been extensively researched due to the rapid development of aerospace industry in the world. For the extreme conditions of working environment, the hot-end components and thermal protect materials were supposed to possess excellent comprehensive properties. ZrB₂-SiC based ceramic, having excellent mechanical properties and oxidation resistance, became one of the most attractive candidate materials in this field.

To further improve the performances of ZrB₂-SiC ceramic, several compounds of refractory metal were added as a third phase, such as MoSi₂^[1], ZrSi₂^[2-3], TaSi₂^[4-5], TaC^[6], WC^[7] and so on. MoSi₂ added in ZrB₂-SiC ceramics was proved to be a good third phase enhancing the sinterability and oxidation resistance. Chamberlain reported the influence of MoSi₂ on the strength of ZrB₂ ceramic which could increased from 565 MPa to 1150 MPa by adding 10vol% MoSi₂^[8]. D. Sciti reported the ZrB₂-MoSi₂ ceramics sintered at 1700-1900°C with hardness of 18.7 ± 0.7 GPa and fracture toughness of 4.0 ± 0.6 MPa·m^{1/2}, the sintering temperature was 300-400 °C lower than ZrB₂ ceramic^[9]. However, ZrB₂-SiC-MoSi₂ ceramic was rarely reported.

In this study, ZrB₂-30vol.%SiC-10vol.%MoSi₂ (Z30S10M) ceramic was prepared by SPS. The microstructure was analyzed by SEM and EDS. The hardness, fracture toughness and bending strengths were measured. At 1500°C, the mass gains oxidized in air with different time were studied, the cross sectional was analyzed to research the oxidation resistance of Z30S10M ceramic. The results provide significant support for the implementation of SPS method in preparing ZrB₂-SiC-MoSi₂ ceramic.

2. Experiment

All the powders used in this study were Commercial. ZrB₂, 10-15μm, 99.5% purity; α-SiC, 2 μm, 99.9 % purity; MoSi₂, 1-3 μm, 99.9 % purity.



2.1. Preparing of Z30S10M ceramic

The volume proportion of three powders is $\text{ZrB}_2\text{:SiC:MoSi}_2 = 70\text{:}30\text{:}10$, they were filled into a ZrO_2 jar to get powder mixtures. After being ball milled with rapid of 200 rpm/min for 6 h taking ZrO_2 ball as media, the slurries were poured out and dried. Then a certain mass of the powder mixtures were placed in a graphite die to sinter in a SPS furnace. With 100°C/min heating rate, the graphite die was heated to 1700°C and held for 5 min under argon atmosphere with 30 MPa pressure, thus the Z30S10M ceramic were obtained.

2.2. Measurement

The density was measured by Archimedeian method. Vickers microhardness (HV 1.0) was obtained on a hardness tester with 9.8 N. Three-point bending strength and fracture toughness with 30 mm span were tested on a bending tester, the head movement rate was 0.5 mm/min. The microstructures were observed using a scanning electron microscopy (SEM), the phase compositions were studied with a energy dispersive spectrometer (EDS). The oxidation resistance experiments were implemented in a tube furnace.

3. Results and Discussions

3.1. Microstructure

SEM images (Fig. 1) show that Z30S10M was comprised of three phases: gray, black and white phase, distributed evenly and there were no aggregation. Very little pores could be observed which was consistent with the relative density (99.8%). The EDS analysis results (Table 1) revealed that ZrB_2 was the gray phase, SiC was the black phase and MoB was the white phase. The XRD pattern further proved the formation of MoB phase (Fig. 2). According to the literatures, the MoB phase was probably formed due to the reaction between ZrB_2 , MoSi_2 and ZrO_2 during sintering^[10-11]. The interphase bonding forces among the phases were enhanced significantly as a result of the formation of MoB which made Z30S10M having good mechanical properties.

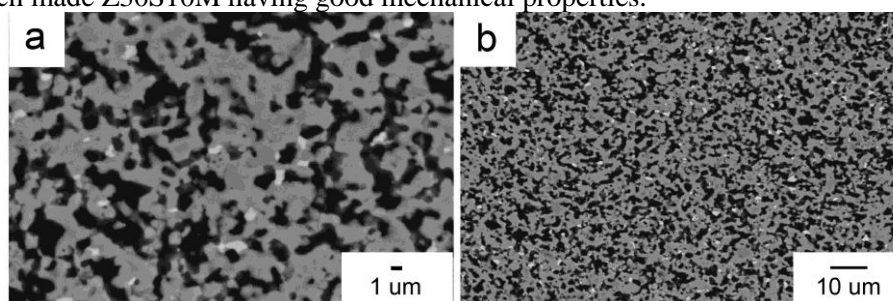


Fig. 1 SEM images of Z30S10M

Table 1 Atomic content of each phase in Z30S10M

Atomic%	White phase	Gray phase	Black phase
Zr	5.36	21.04	0.10
O	--	0.03	0.72
Mo	35.37	0.70	--
Si	0.94	0.61	40.54
C	1.67	1.40	53.15
B	56.67	76.22	5.49

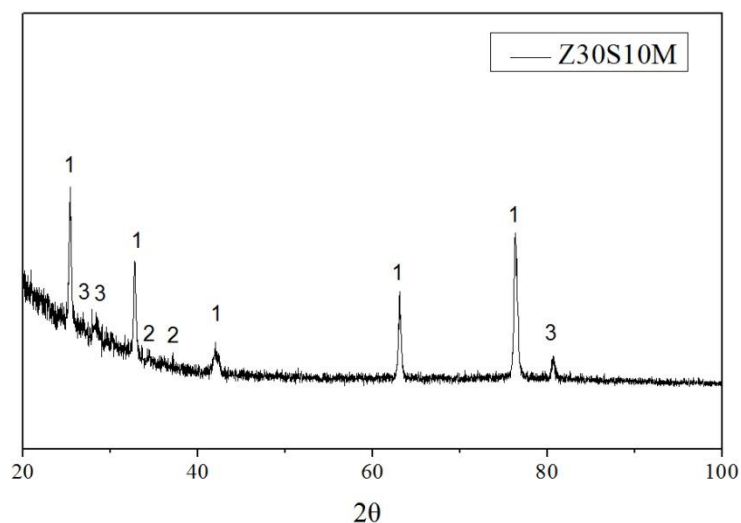


Fig. 2 XRD pattern of Z30S10M

3.2. Mechanical properties

The hardness, fracture toughness and bending strengths at different temperature were tested and shown in Table 2. The fracture toughness of Z30S10M was about $5.73 \text{ MPa m}^{1/2}$. The hardness was 16.1 GPa. The bending strength at room temperature, 1600 °C and 1800 °C were 428 MPa, 66 MPa and 22 MPa, respectively. Due to the soften of grain boundaries at high temperature, bending strength decreased significantly.

Table 2 Fracture toughness, hardness and bending strengths of Z30S10M

Sample	Fracture toughness at room temperature ($\text{MPa m}^{1/2}$)	HV0.5 (GPa)	Bending strength (MPa)		
			25 °C	1600 °C	1800 °C
Z30S10M	5.73	16.1	428	66	22

The cross sectional fracture morphology of Z30S10M was observed by SEM (Fig.3). The results showed that it fractured with both intergranular and transgranular mixed mode. A lot of smooth cleavage surfaces on the cross section indicated that the fracture mode was predominantly transgranular. A small amount of particle pull-out showed that ceramic was toughening by adding MoSi_2 .

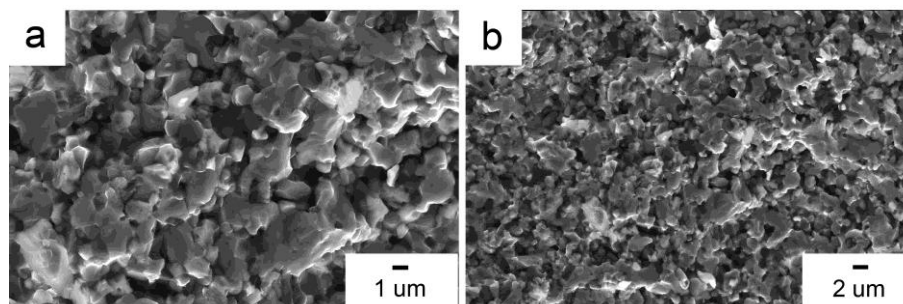


Fig. 3 Cross sectional SEM images of Z30S10M fractured at room temperature

3.3. Oxidation resistance

Z30S10M was oxidized at 1500 °C by different time in air to investigated the oxidation resistance. The images of oxidized samples were shown in Fig.4. A thin and transparent SiO_2 oxide layer with some

fine bubbles was formed on the surface of Z30S10M when oxidizing for 1h. The bubbles were caused by the volatile oxide produced during oxidization, such as B_2O_3 and CO. With prolonging the oxidization time, the SiO_2 oxide layer got thicker and thicker and the bubbles got larger. After oxidizing for 10 h, the SiO_2 oxide layer turned white and the oxide bubbles got broken.

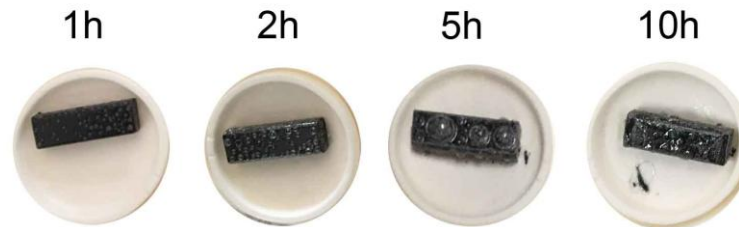


Fig. 4 Z30S10M samples oxidized at 1500 °C by different time in air

Table 3 Mass gain of Z30S10M oxidized at 1500 °C by different time in air

Sample	Mass gain (mg/cm^2)				
	1 h	2 h	5 h	8 h	10 h
Z30S10M	3.53	4.74	9.01	12.65	14.42

The mass gains of Z30S10M oxidized at 1500 °C by different time in air were listed in Table 3. At the early stage(0-1h), the mass gain grew fast to $3.53 mg/cm^2$. After 1h, The growth rates of mass gain got slow down. After being oxidized for 10h, the mass gain of Z30S10M was about $14.42 mg/cm^2$ indicated that Z30S10M had good oxidation resistance in air at 1500 °C.

The cross sectional SEM image of Z30S10M oxidized in air for 10 h at 1500 °C was analyzed. The O, Si, B, Mo, Zr element mappings at the same area were shown in Fig.5. Combining with the literature^[12], the oxidation layer of Z30S10M consisted of three layers: rich SiO_2 layer, rich ZrO_2 layer, SiC depletion layer. During the oxidation process, SiO_2 produced by oxidizing of SiC evaporated to the surface to form rich SiO_2 layer (62 μm). Porous rich ZrO_2 layer (260 μm) was formed in situ by oxidizing of ZrB_2 (B_2O_3 evaporated). The unreacted O infiltrated into the substrate to react with SiC to form SiC depletion layer (38 μm). The rich SiO_2 layer on the surface could prevent further infiltration of oxygen and mitigate the oxidation rate. The thickness of oxide scale (total thickness of three layers) was about 360 μm . The oxidation depth was about 298 μm (sum of the thicknesses of rich ZrO_2 layer and SiC depletion layer, obtained by diffusion depth of O element,), which could stand for the oxidation degree. The results suggested that Z30S10M had good oxidation resistance.

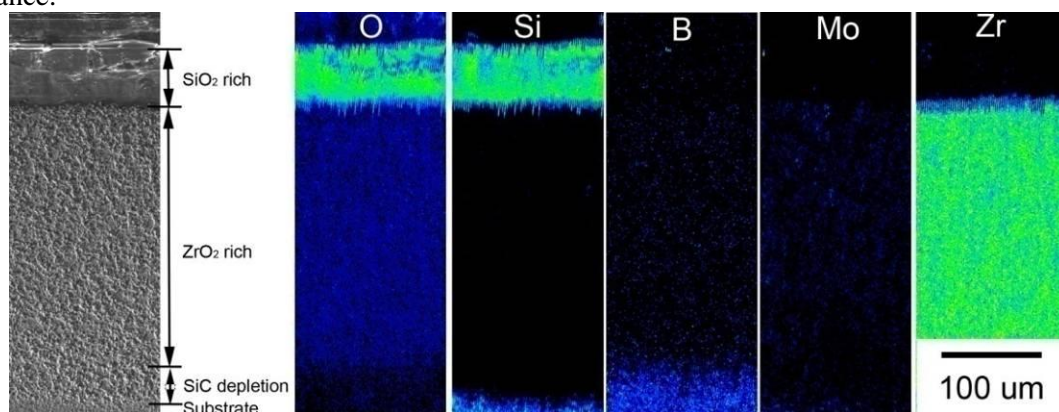


Fig. 5 Cross sectional SEM image of oxidized Z30S10M and the O, Si, B, Mo, Zr element mappings at the same area

4. Conclusions

ZrB₂-30vol.%SiC-10vol.%MoSi₂ ceramic was successfully fabricated via SPS method at 1700 °C. MoB phase enhancing the interphase bonding forces was generated during SPS. The mechanical properties were excellent that the fracture toughness, hardness and bending strength were 5.73 MPa m^{1/2}, 16.1 GPa and 428 MPa, respectively. Besides, it has good oxidation resistance, the mass gain oxidizing at 1500 °C for 10 h was about 14.42 mg/cm², the oxidation depth was about 298 μm.

References

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