

Densification, microstructure and hardness of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites

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The densification behaviour of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites was studied by pressureless sintering at temperatures of 1500–1700 °C for 10 h in air. The microstructure and hardness of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites were investigated by the X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy and Vickers hardness tester. The $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites are composed of pyrochlore-type $\text{Sm}_2\text{Zr}_2\text{O}_7$ and perovskite-like SmAlO_3 structure. The relative density of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites increases with increasing sintering temperature. Vickers hardness of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites slightly increases with increasing SmAlO_3 content.

Key words: Ceramics, Sintering, Microstructure, Hardness.

Introduction

In recent years, oxide materials with the general formula of $\text{A}_2\text{B}_2\text{O}_7$ (A = lanthanide, B = Zr, Hf, Ce, Sn, Ti, etc.) have received considerable attention. These compounds exhibit a pyrochlore-type structure or a defect fluorite-type structure, which is mainly governed by the ionic radius ratio of A^{3+} and B^{4+} [1]. The pyrochlore-type structure belongs to the space group $\text{Fd}3m$ (227), while the fluorite-type structure has the space group $\text{Fm}3m$ (225). They have a wide variety of interesting physical and chemical properties, such as high-melting point, high thermal expansion coefficient, low-thermal conductivity, high thermal stability, high photocatalytic activity and high-radiation stability. These properties make them suitable for applications in advanced technologies such as refractory materials, high-temperature thermal barrier coating materials, catalysts, nuclear waste forms, etc. [2–7]. $\text{Sm}_2\text{Zr}_2\text{O}_7$ is one of the $\text{A}_2\text{B}_2\text{O}_7$ -type compounds and well-known of its good phase stability (>2000 °C), low thermal conductivity ($1.62 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, 1200 °C) and high thermal expansion coefficient ($11.9 \times 10^{-6} \text{ K}^{-1}$, 1200 °C) [8–10]. Therefore, $\text{Sm}_2\text{Zr}_2\text{O}_7$ is believed to have potential applications as a high temperature thermal barrier coating material over 1200 °C. Recently, $\text{Sm}_2\text{Zr}_2\text{O}_7$ coatings were successfully prepared by electron-beam evaporation, directed-vapor deposition and air plasma spraying techniques [11, 12], respectively. However, the thermal cycling life of pyrochlore-type coatings is not improved in comparison with 6–8 wt.% Y_2O_3 - ZrO_2 coatings because of the formation of perovskite phase due to chemical reaction between the

pyrochlore phase and the thermally grown oxide Al_2O_3 [13]. The phase diagram of alumina-zirconia-samarium system was constructed in a temperature range of 1250–2800 °C by Lakiza *et al.* [14, 15]. Fabrichnaya *et al.* assessed the thermodynamic parameters of alumina-zirconia-samarium system using Calphad approach [16]. However, there is a paucity of microstructure and property of alumina-zirconia-samarium system for potential high temperature applications. $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites will be a part of the alumina-zirconia-samarium system. In this work, $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites were prepared by pressureless sintering process. The densification, microstructure and hardness of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites were further investigated.

Experimental

In the present study, $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites were prepared by conventional solid state reaction technique using zirconia, alumina (Dongguan SG Ceramics Technology Co. Ltd, China; purity $\geq 99.9\%$) and samaria (Grrem Advanced Materials Co., Ltd., China; purity $\geq 99.9\%$) powders. All raw powders were

Table 1. Original composition of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites used in this investigation.

Sample codes	Composition (mol.%)		
	ZrO ₂	SmO _{1.5}	AlO _{1.5}
S1	40	50	10
S2	37.5	50	12.5
S3	33.3	50	16.7
S4	28.6	50	21.4
S5	25	50	25

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calcined at 900 °C for 2 h in air before further use. Original composition of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites (designated with the sample codes of S1-S5, respectively) used in this investigation are presented in Table 1. Appropriate amounts of zirconia, samaria and alumina powders were homogenized using zirconia balls and analytically pure alcohol. The mixed powders were compacted into pellets by uniaxial and isostatic pressing at 20 MPa and 200 MPa, respectively. The pellets were cylindrical with the dimensions of 25 mm in diameter and 5 mm in height and with a green density of about 45% theoretical density. Sintering experiments were carried out in air using the cold isostatically pressed pellets in the temperature range of 1500–1700 °C. The pellets were held for 10 h at sintering temperature and then furnace cooling to room temperature.

The bulk density of the sintered composites was measured by the usual volume and weight measurement technique. The phase structure of sintered composites was identified by an X-ray diffractometer (Rigaku D/MAX 2200VPC, Japan) with $\text{Cu K}\alpha$ radiation at a scanning rate of 5°/min at room temperature. The microstructure of the as-sintered ceramic composites was observed by a scanning electron microscope (FEI Quanta 200F, the Netherlands) equipped with energy-dispersive X-ray spectroscopy operating at 20 kV. A thin carbon

coating was evaporated onto the surface of the sample for the electrical conductivity. Vickers hardness was measured by a hardness tester (HVS-30, China) with an applied load of 98 N and holding time of 15 s.

Results and Discussion

Figure 1 reveals XRD patterns of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites sintered at different temperatures for 10 h in air. No distinct influence of sintering temperature on phase constituents is found in the sintering temperature range of 1500–1700 °C. $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites are composed of pyrochlore-type $\text{Sm}_2\text{Zr}_2\text{O}_7$ and perovskite-like SmAlO_3 structure, which can be indexed using JCPDS files no. 24-1012 and 71-1597, respectively. Figure 2 shows the variations in the relative density of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites sintered at different temperatures for 10 h in air. Clearly, the relative density increases rapidly with increasing sintering temperature for all compositions. All samples sintered at 1500 °C have a low relative density of 66–73%. However, the samples sintered at 1700 °C reach a relative density of more than 95%.

Figure 3(a) and (b) shows the typical surface morphology of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites sintered at 1500 °C for 10 h in air. It is clearly seen that there are many pores in $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic

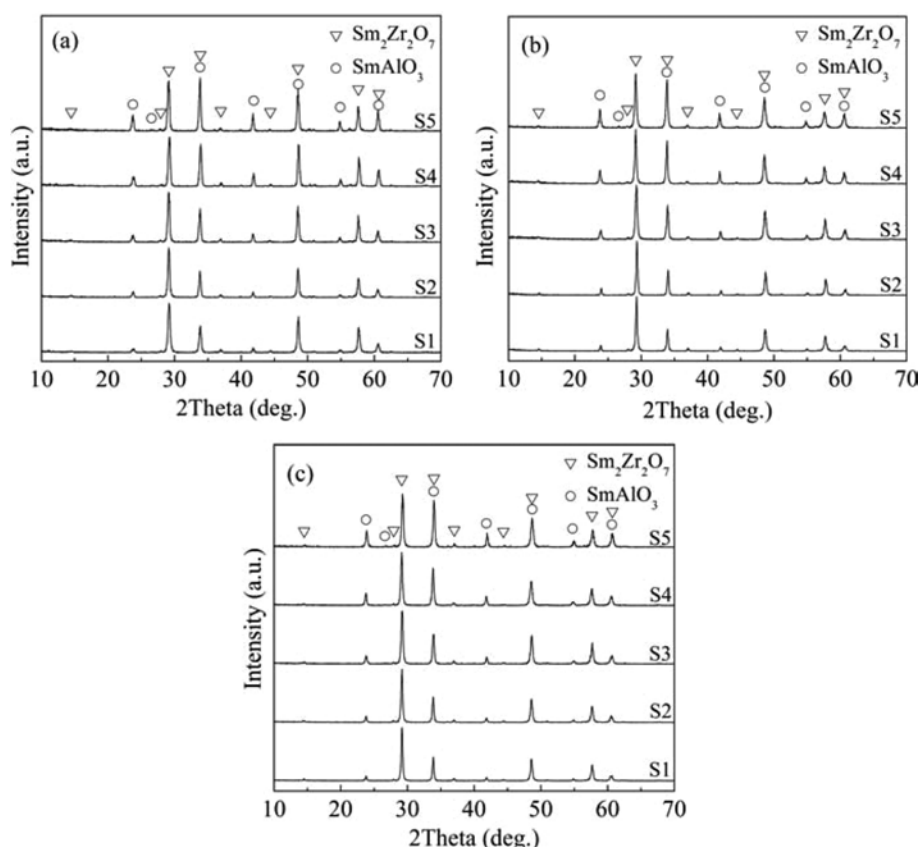


Fig. 1. XRD patterns of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites sintered at different temperatures for 10 h in air: (a) 1500 °C, (b) 1600 °C, (c) 1700 °C.

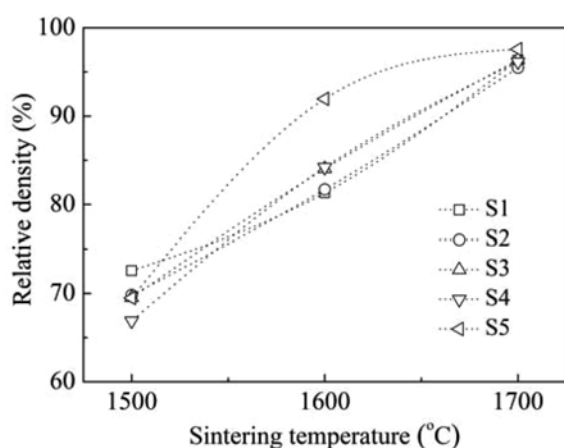


Fig. 2. Relative density of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites as a function of sintering temperature.

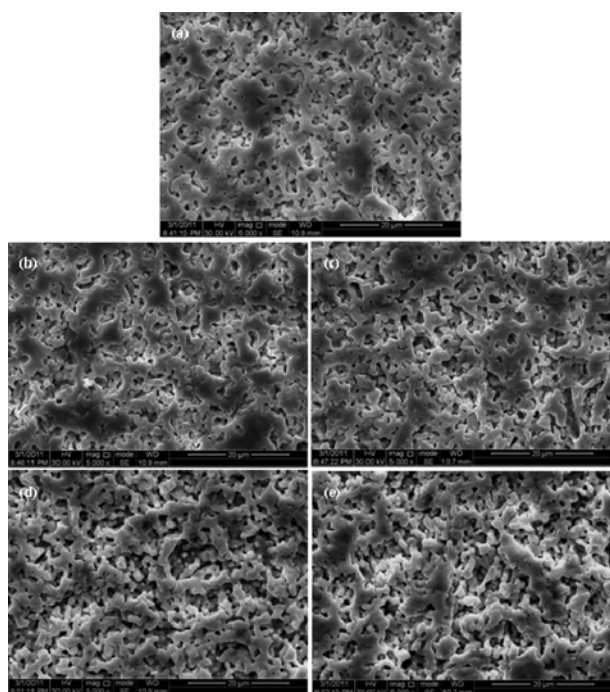


Fig. 3. Surface morphologies of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites sintered at 1500 °C for 10 h in air: (a) S1, (b) S2, (c) S3, (d) S4, (e) S5.

composites due to their low relative density. The SEM micrographs shown in Fig. 4 reveal the surface morphology of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites sintered at 1600 °C for 10 h in air. There exist some local dense areas compared with the samples sintered at 1500 °C. Figure 5 displays the surface morphologies and EDS spectra of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites sintered at 1700 °C for 10 h in air. The $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites show two kinds of typical features, which are composed of large $\text{Sm}_2\text{Zr}_2\text{O}_7$ grains and small SmAlO_3 grains, as confirmed from the EDS analysis in Fig. 5(f) and (g). According to the EDS analysis, the approximate mole ratio of different metallic elements at selected locations of A and B in Fig. 5(d) is shown in Table 2.

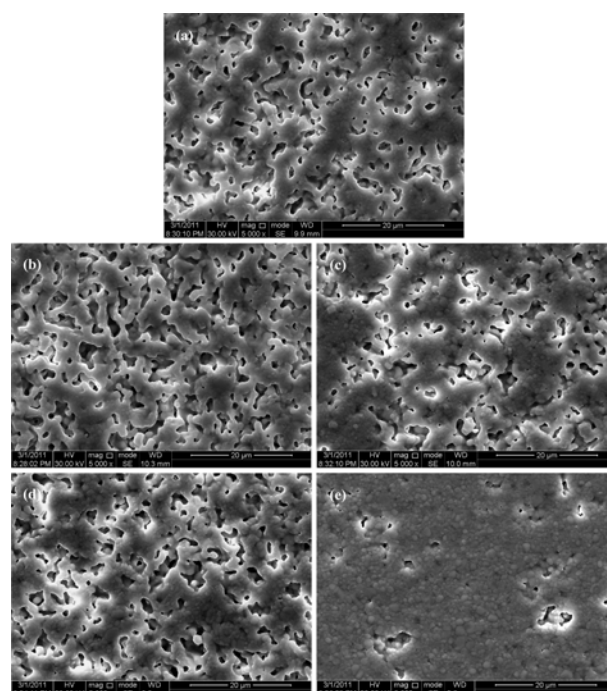


Fig. 4. Surface morphologies of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites sintered at 1600 °C for 10 h in air: (a) S1, (b) S2, (c) S3, (d) S4, (e) S5.

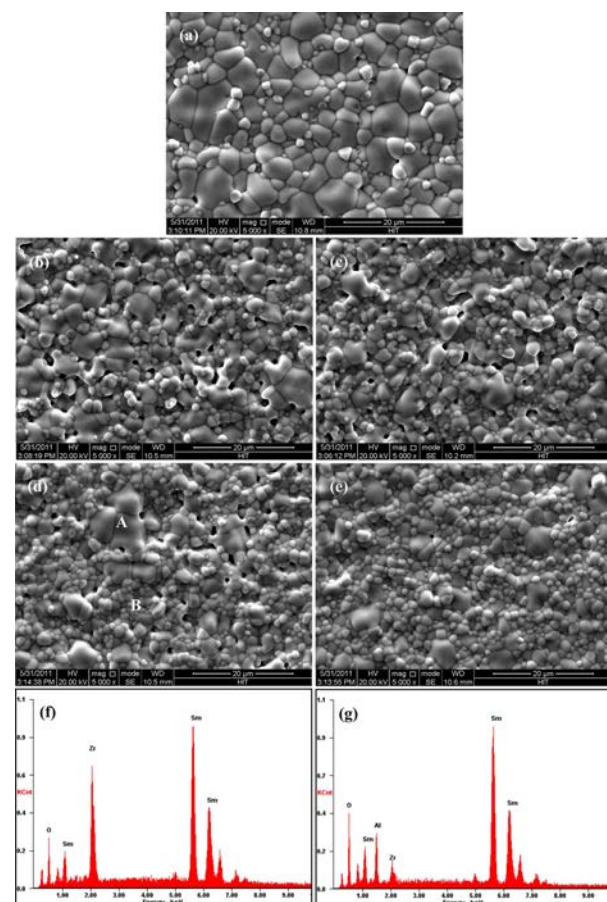
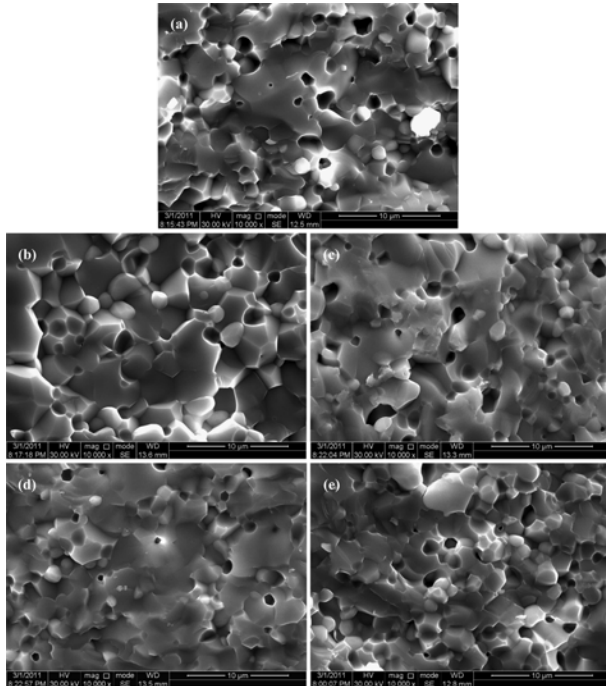
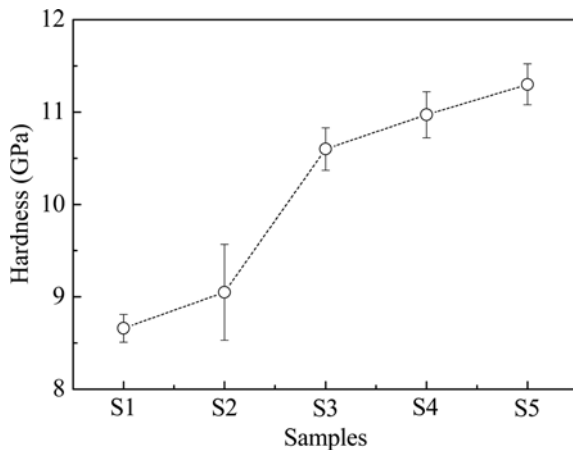


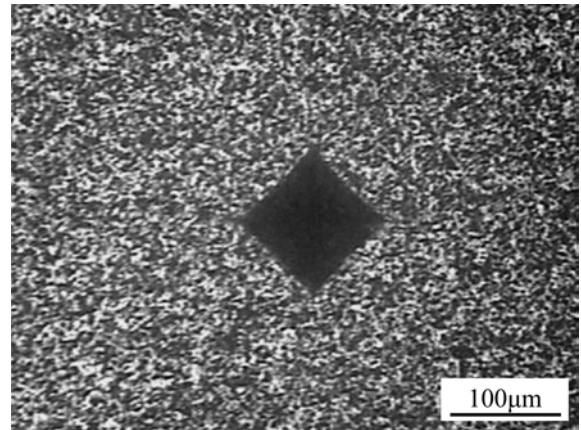
Fig. 5. Surface morphologies and EDS spectra of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites sintered at 1700 °C for 10 h in air: (a) S1, (b) S2, (c) S3, (d) S4, (e) S5, (f) and (g) EDS spectra at the locations of A and B in (d), respectively.

Table 2. Chemical compositions at selected locations of A and B in Fig. 5(d) detected by EDS.

Locations	Mol ratio		
	Zr	Sm	Al
A	50.3	49.7	0
B	5.2	49.7	45.1

**Fig. 6.** Cross-section morphologies of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites sintered at 1700 °C for 10 h in air: (a) S1, (b) S2, (c) S3, (d) S4, (e) S5.**Fig. 7.** Vickers hardness of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites sintered at 1700 °C for 10 h in air.

With increasing sintering temperature, different diffusion mechanisms such as grain boundary diffusion, bulk diffusion and surface diffusion, etc. contribute to the densification process during sintering [17]. The pores become less and less, and the bulk ceramics become denser and denser, especially after sintering at 1700 °C. It is clearly seen from Figs. 3-5 that the average grain size

**Fig. 8.** Typical Vickers indentation of the sample S5 sintered at 1700 °C for 10 h in air.

of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites obviously increases with increasing sintering temperature. Figure 6 shows the cross-section morphologies of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites sintered at 1700 °C for 10 h in air. There are both large $\text{Sm}_2\text{Zr}_2\text{O}_7$ grains and small SmAlO_3 grains, which is consistent with the surface morphologies as shown in Fig. 5.

Vickers hardness of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites sintered at 1700 °C for 10 h in air is shown in Fig. 7. The values of Vickers hardness in Fig. 7 are the arithmetic means of seven measurements. The error derived from the mean standard deviation of seven measurements for each sample is presented in Fig. 7. It can be seen that Vickers hardness of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites slightly increases from the sample S1 to S5, which is probably owing to the relatively high hardness of the SmAlO_3 phase. Figure 8 is the typical Vickers indentation of the sample S5 sintered at 1700 °C for 10 h in air. It is clearly seen that the Vickers indentation exhibits a four pyramid shape.

Conclusions

$\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites sintered at temperatures of 1500-1700 °C for 10 h in air are composed of pyrochlore-type $\text{Sm}_2\text{Zr}_2\text{O}_7$ and perovskite-like SmAlO_3 structure. The relative density of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites increases with increasing sintering temperature and reach above 95% when sintered at 1700 °C for 10 h in air. Vickers hardness of $\text{Sm}_2\text{Zr}_2\text{O}_7/\text{SmAlO}_3$ ceramic composites slightly increases with increasing SmAlO_3 content.

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