

Effects of SnO₂ Addition on the Synthesis of Magnesium Aluminate Spinel Microplatelets

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In order to prepare platelet-like spinel expected as the reinforcing phase, different amounts (5–20 at %) of SnO₂ were added into the mixture of magnesia and alumina platelets, and then heated at 1300–1600 °C for 5 h. Effects of SnO₂ addition on the synthesis of magnesium aluminate spinel microplatelets were investigated. The synthesized spinel was characterized by X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy. Spinel platelets like “sesame cookie” formed derived from platelet alumina based on the template process. The highest spinel content in samples with 10 % of SnO₂ addition achieved. The amount of Al₂O₃ and SnO₂ in solid solution and degree of orderliness for spinel depended on SnO₂ addition.

Keywords: tin oxide, magnesium aluminate spinel, microplatelets.

1. INTRODUCTION

Magnesium aluminate spinel (MAS) was called as “mullite in 21st century” because of high melting point (2105 °C), good mechanical strength (110–245 MPa), low thermal expansion coefficient ($10.2 \times 10^{-6}/^{\circ}\text{C}$ at 1500 °C) and high corrosion resistance [1, 2]. MAS platelets mostly were prepared by vapor-phase reaction, molten salt synthesis and hydrothermal treatment, which could be used as reinforcing phases in ceramic matrix composites [3–5]. The generated spinel lost the hexagonal shape if Al₂O₃ platelets and MgO powder with equimolar ratio were calcined at 1400 °C for 3 h [6]. However, the reaction between alumina and magnesia was slowed down due to the associated volumetric expansion [7]. In general, a small amount (less than 1 %) of the mineralizer was added to promote the formation and densification of MAS [8, 9]. SnO₂ as a spinel forming agent could accelerate the formation of spinel [10]. Moreover, the properties of MgO-spinel and spinel-based castables were increased markedly by incorporation of SnO₂ [11, 12]. Based on bioinspired approaches, the toughness and strength of ceramics by inducing platelet-like phases were unexpectedly high [13–15]. The flexural strength of alumina platelets has been measured as 5.3 GPa [16]. The synthesis of the platelet-like phase was crucial to achieve the fore mentioned properties. The aim of this work is to evaluate and analysed the effect of SnO₂ addition on synthesize magnesium aluminate spinel microplatelets from the mixture of magnesia and alumina platelets. MAS platelets synthesized with different SnO₂ amounts and the temperatures were characterized.

2. EXPERIMENTAL DETAILS

Magnesium aluminate spinel was synthesized using alumina platelet (Aladdin, $d_{50} = 9.5 \mu\text{m}$, analytical grade), magnesia (Aladdin, $d_{50} = 4.7 \mu\text{m}$, 98 %) and tin oxide (Shanghai Zhanyun Chemical, $d_{50} = 1.2 \mu\text{m}$, chemically pure) as starting materials. The addition of SnO₂ varied from 0 to 20 at % as shown in Table 1. The samples with SnO₂ of 0, 5, 10 and 20 at % were denoted as S0, S5, S10 and S20, respectively. Raw materials and ethanol were mixed with a ratio of 1 g : 1 ml using a planetary mill for 4 h. After drying at 110 °C, the mixture of raw materials was uniaxially pressed at 100 MPa into discs with 20 mm diameter and 20 mm height. The samples were heated up to 1000 °C at the heating rate of 7 °C/min, and then calcined at the heating rate of 5 °C/min to the holding temperature. Finally, the samples were soaked at the temperature of 1300, 1400, 1500 and 1600 °C for 5 h in air, respectively. The calcined samples were weighed for calculating the mass loss.

Table 1. Chemical composition of samples (at %)

	Al ₂ O ₃	MgO	SnO ₂
S0	50	50	–
S5	47.5	47.5	5
S10	45	45	10
S20	40	40	20

The phase compositions of samples were determined by X-ray diffraction (XRD, Philips, X'pert Pro MPD, Netherlands) with CuK_α radiation. The spinel content was calculated by using RIR method [17]. The microstructure of products was characterized by scanning electron microscopy (SEM, JEOL, JSM-6610, Japan) and energy dispersive spectrometer (EDS, Bruker, QUANTAX200-30, Germany).

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3. RESULTS AND DISCUSSION

The mass loss of samples after calcined at 1300–1600 °C for 5 h is presented in Fig. 1. Due to the sublimation of tin oxide, the mass loss of samples S10 and S20 was larger than that of S0 and S5 when the calcining temperature was above 1400 °C. The maximum of mass loss for sample S20 calcined at 1600 °C reached 24 %, which implied that about 70 % SnO₂ vanished.

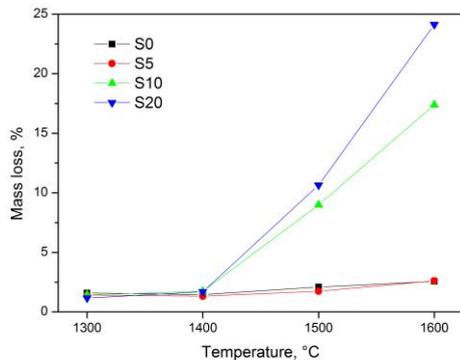


Fig. 1. Mass loss of samples calcined at 1300–1600 °C for 5 h

Fig. 2 shows XRD patterns of samples after calcining at 1300–1600 °C for 5 h. For reference sample S0, alumina reacted gradually with magnesia with the calcining temperature. The unreacted magnesia still presented in sample S0 after calcined at 1600 °C. But there were Mg₂SnO₄, unreacted Al₂O₃ and MgO in sample S5.

Except for SnO₂ and trace MgO, spinel was predominant in sample S10 after calcined at 1600 °C. Mg₂SnO₄ and excess SnO₂ existed in sample S20 calcined at all temperatures. The results of semi-quantity analysis are plotted in Fig. 3. The spinel content in sample S10 was the maximum. While the generated spinel in sample S20 was the least amount due to the formation of Mg₂SnO₄ and the rest of Al₂O₃ and SnO₂. Considering the yield of spinel, the addition of 10 at % SnO₂ was optimal. The order of effective SnO₂ addition from less to more after calcining at 1600 °C was S10, S5 and S20 by deducting the amount of the sublimation. Therefore, the highest conversion rate was achieved when a small amount of SnO₂ was added. More SnO₂ led to form Mg₂SnO₄, which inhibited the formation of spinel.

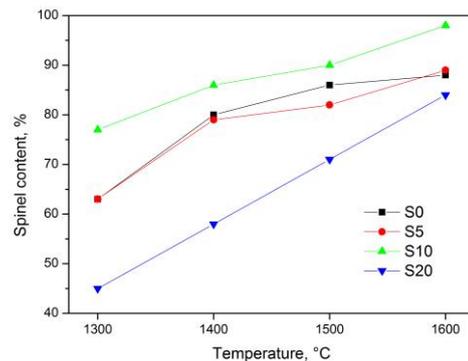


Fig. 3. Spinel content of samples calcined at 1300-1600 °C for 5h

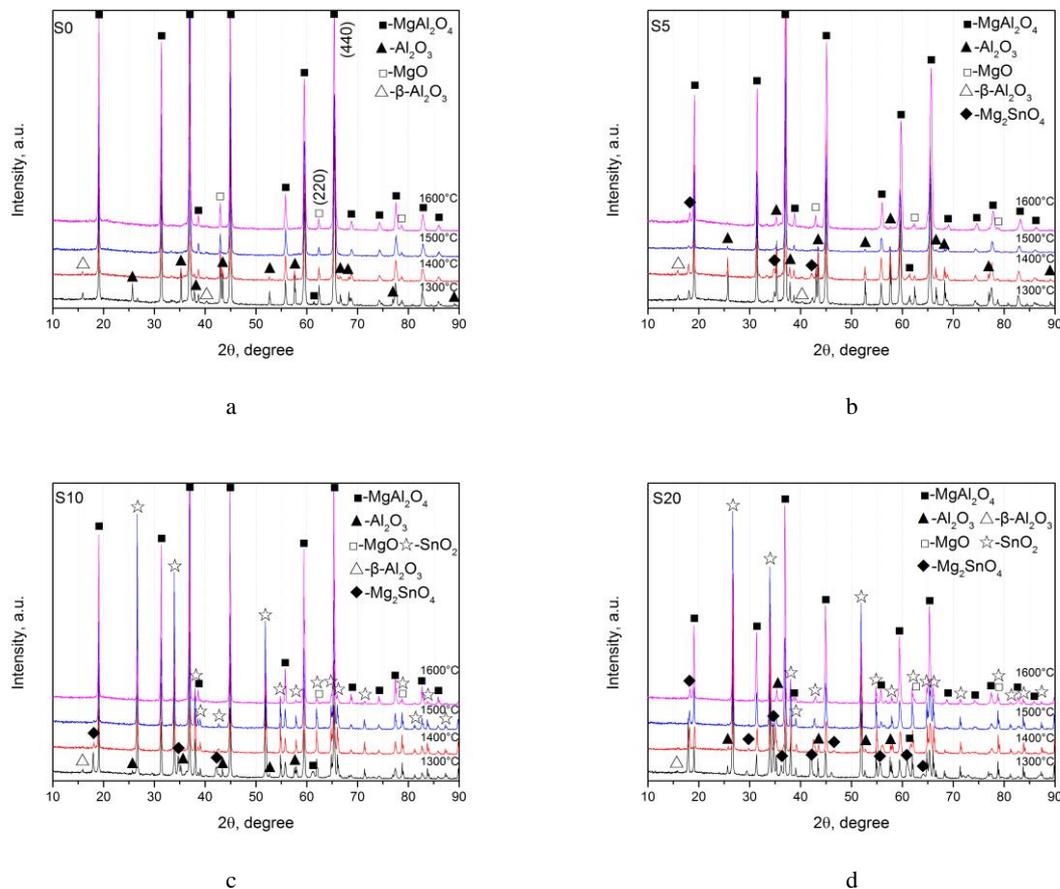


Fig. 2. XRD patterns of samples calcined at 1300–1600 °C for 5 h: a–S0; b–S5; c–S10; d–S20

Selecting MgO (220) peak as the reference, the changes of the diffraction peak's position (440) for spinel are shown in Fig. 4.

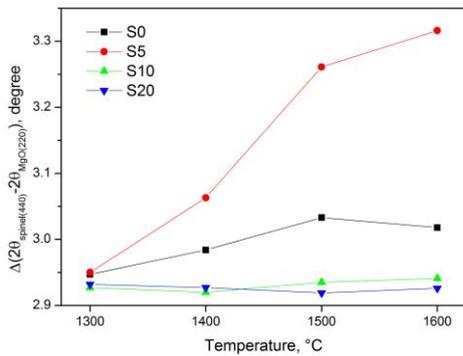


Fig. 4. Relative position of diffraction peaks (440) for spinel in samples calcined at 1300–1600 °C for 5 h

As a consequence of the reaction among the raw materials, the composition of spinel varied with the temperature and SnO₂ addition. The spinel peak shifted to higher angle in sample S0 without SnO₂, which indicated that Al-rich spinel formed with the calcining temperature. It was deduced that more alumina dissolved into spinel in sample S5 because the formation of Mg₂SnO₄ consumed more MgO. In contrast, the spinel peak's position changed little, which demonstrated that the reaction of Al₂O₃ and MgO with equal molar ratio may happen in sample S10. Another possibility is to form a solid solution containing a small amount of SnO₂, which caused lattice defects with the formation of ionic vacancies, thereby promoting the spinel formation [18]. More tin element entered the lattice of spinel, which accounted for the similar change of spinel's peak for sample S20. These results were in accordance with the reference [19], which mentioned that

the stoichiometric spinel could produce when raw materials including Al₂O₃, MgO and SnO₂ were balanced.

Normally, Mg and Al cation occupied tetrahedral and octahedral site respectively in perfect magnesium aluminate spinel [20]. The degree of disorder for the spinel structure depended on the calcination temperature. By comparing the peak intensity of {311} and {400}, the degree of order for the spinel phase could be calculated using the equation as $I_O/(I_O + I_D)$ [21]. I_O and I_D stood for intensity of order and disorder phase respectively. Specifically, I_O = intensity of {311} plane, and I_D = intensity of the disorder spinel phase in {400} plane. From Fig. 5, the degree of spinel's orderliness reached the maximum for all samples after calcined at 1500 °C. The spinel in samples containing SnO₂ basically presented higher orderliness than the reference.

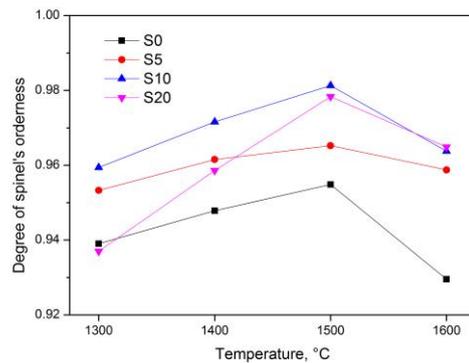


Fig. 5. Degree of spinel's orderliness in samples calcined at 1300–1600 °C for 5 h

SEM images of samples obtained with different SnO₂ additions as well as alumina platelets are shown in Fig. 6.

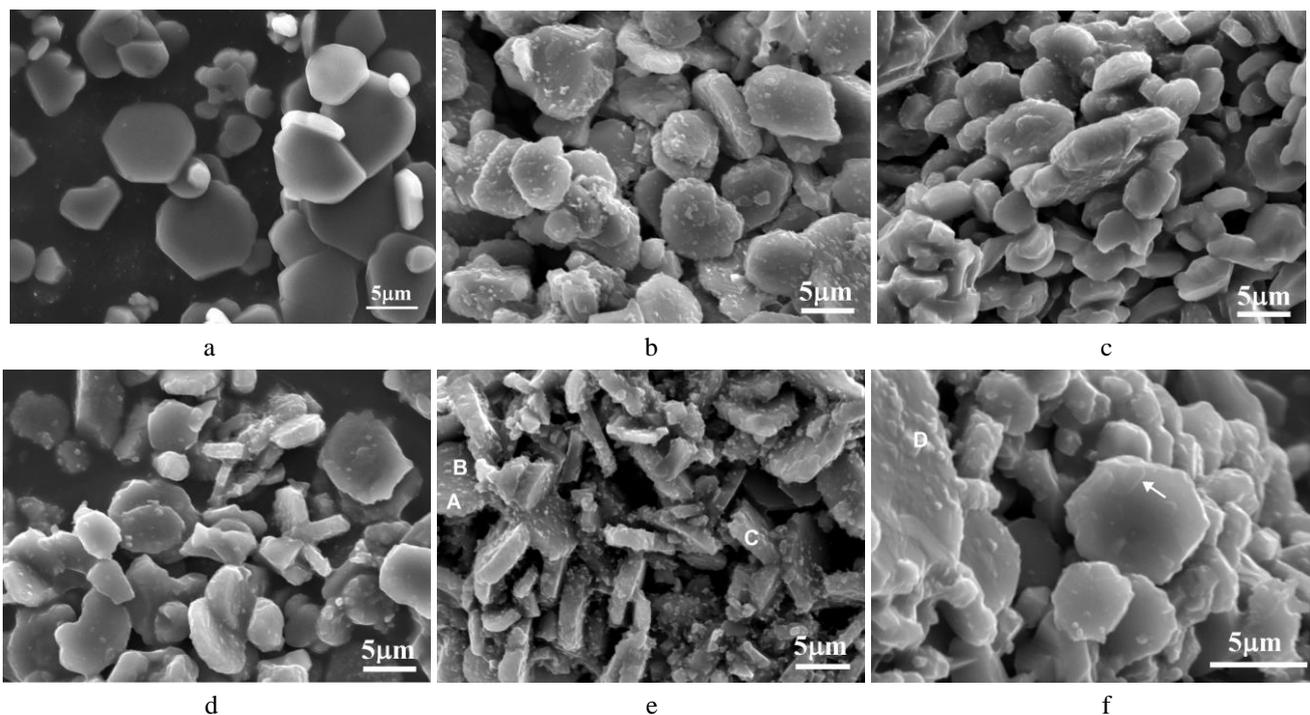


Fig. 6. SEM images of alumina platelets (raw material): a– and samples calcined at 1600 °C for 5 h; b–S0; c–S5; d–S10; e, f–S20)

The majority of spinel maintained the morphology of the alumina platelets because of the faster magnesia diffusion [22]. The ratio of the formed spinel layers located at the Al₂O₃ side to the MgO side increased with the composition and temperature [5]. Therefore, there were a lot of ridges on the rough surface of the spinel platelets liking “sesame cookie” (Fig. 6 b–f). By comparison, the original surface of alumina platelets in raw materials was smooth (Fig. 6 a). The chemical composition of the different regions was identified by EDS (Table 2). The ridges on the surface contained more tin than the inner of spinel. This kind of heterogeneous structure needs to be investigated further. The growth stage (marked by an arrow) also can be seen on the surface of spinel (Fig. 6 f).

Table 2. Chemical composition of areas determined by EDS

Element, at %	O	Al	Mg	Sn
A	60.4	27.1	12.3	0.2
B	61.5	26.9	11.4	0.3
C	58.9	28.2	12.9	0.1
D	53.2	31.8	14.4	0.5

4. CONCLUSIONS

The addition of SnO₂ was effective to accelerate the formation of spinel microplatelets derived from platelet alumina. The spinel content as well as its orderliness in the sample with 10 at % SnO₂ addition achieved the maximum by combined effects of SnO₂. Due to the higher diffusion rate of magnesia, the spinel platelets with “sesame cookie” structure formed.

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