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Pressureless sintered magnesium aluminate spinel with enhanced mechanical properties obtained by the two-step sintering method

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ABSTRACT

The effects of sintering parameters, first and second step sintering temperatures (T_1 and T_2, respectively), on the microstructure of magnesium aluminate spinel (MAS) were investigated. A single-step sintering (SSS) method was used to determine the appropriate temperatures for the first step. Different two-step sintering (TSS) regimes were used to investigate the effect of second step sintering temperatures on densification behavior and grain growth. The results show that, by using SSS method, the densification kinetics of MAS is different from grain growth kinetics. A MAS material with a high relative density of 96.17% and a homogeneous microstructure consisting of small grains (680 nm) is achieved under optimum TSS conditions ($T_1 = 1650$ °C/0 h and $T_2 = 1550$ °C/10 h). Compared with conventional specimen, the bending strength (240 MPa) and Vickers hardness (11.05 GPa) of the sintered samples fabricated under optimum TSS increased by 54.8% and 52.2%, respectively.

1. Introduction

Magnesium aluminate spinel (MAS) is a very interesting ceramic material due to its properties like high melting point (2035 °C), good mechanical strength at low and high temperatures, low thermal expansion and dielectric constant, and chemical inertness [1,2] which make MAS suitable for a wide range of industrial applications. In the past, sintering of MAS was performed by conventional pressureless sintering. This process is normally performed at above 1900 °C to obtain dense spinel, but this densification is usually accompanied by exaggerated grain growth. Pressureless sintering of MAS at lower temperature would be desirable in order to limit the grain growth, but it is still an unresolved issue. The final grain size and density of sintered products can be influenced by the choice of sintering regimes [3]. Substantial researches have been conducted to reduce the grain size by choosing a correct sintering cycle, such as rapid rate sintering [4] and two-step sintering [5,6]. Rapid rate sintering processes such as spark plasma sintering [7] and microwave sintering [8] have already been used to obtain high density and ultrafine grain ceramics. However, this method is limited by high production costs and the need for sophisticated equipment [9]. Compared with the rapid rate sintering, two-step sintering is a simple way to obtain a material with a high relative density and a homogeneous microstructure consisting of small grains.

In 2000, Chen and Wang [5] developed a two-step sintering (TSS) method for Y_2O_3 densification. This method is a promising approach to obtain fully dense nano-grained ceramics. In the TSS method, the sample is first heated to a high temperature (T_1) to achieve a critical density and to render its pores unstable. The sample is then immediately cooled at a sharp rate to a lower temperature (T_2) and maintained at that temperature for a long time to achieve fully dense fine-grained materials. This method has also been applied to various materials, such as $Ca_3MgSi_2O_8$ [10], $Cu(In_{0.7}Ga_{0.3})Se_2$ [11], ZrO_2 [12], $NiFe_2O_4$ [13], ZnO [14,15], Al_2O_3 [16,17], $BaTiO_3$ [18], $Ca_{10}(PO_4)_6(OH)_2$ [19] and $(K_xNa_{1x})_{0.94}$-$Li_{0.06}NbO_3$ lead-free ceramic [20]. However, only few studies have reported the preparation of dense and fine MAS ceramics by TSS method.

According to previous studies [21,22], TSS attentions have focused on the choice of sintering temperature, T_1 and T_2, and grain growth behavior during the second step of sintering. In this paper, a TSS method is applied to MAS sintering to achieve a dense and fine structure. The effects of temperature on densification and grain growth are discussed. Bending strength and hardness of two-step sintered samples are also reported. Meanwhile, a comparison is made with the conventional pressureless sintering regime.

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2. Experimental

2.1. Preparation of MAS powders and green compacts

Mixed solution of stoichiometric magnesium and aluminum chlorides with Mg^{2+}:Al^{3+} molar ratio 1:2 was prepared by dissolving the corresponding amount of magnesium and aluminum chlorides in 80 °C distilled water. After mixing the corresponding chlorides, these solutions were stirred with an excess of NH_4OH solution at pH 9.5–10.5 [23]. The gelatinous precipitate was finally dried overnight at 120 °C and then calcined at 1200 °C for 2 h with a heating rate of 3 °C/min.

Cylindrical samples (Φ20 mm × 8 mm) and bar samples (5 mm × 6 mm × 50 mm) were fabricated under a uniaxial pressure of MAS powders at 200 MPa for 3 min in air at room temperature.

2.2. Sintering

Sintering of the samples was carried out through conventional sintering (CS) and TSS methods. CS was carried out in air at a peak temperature (T) with a heating rate of 3 °C/min and then furnace cooled to room temperature.

Two preliminary sintering tests were undergone to determine the sintering parameters of TSS. One test consisted of a single-step sintering (SSS) which was used to determine the T_1 of the TSS. In this test, the SSS was carried out at 1400–1750 °C (T_1) in air with 50 °C temperature intervals and a heating rate of 10 °C/min. The sample was heated to the maximum temperature (T_1) without any holding time and then cooled down to room temperature. Linear shrinkage data was calculated by comparing the diameters of sintered and pressed cylindrical samples. The linear shrinkage rate was obtained by differentiating the measured linear shrinkage data. Another test was carried out by the TSS. The heating rate was 10 and 5 °C/min below and above 1400 °C, respectively. The specimens were then cooled at 30 °C/min to a lower temperature T_2 and held there for isothermal sintering with a holding time of 10 h. Time and temperature conditions as well as heating and cooling rates in conventional sintering and two-step sintering procedures are compared in Fig. 1.

2.3. Characterization

Bulk density of the sintered products was measured by the conventional liquid displacement method using Archimedes' principle. Phase analysis was done by X–ray diffraction technique (by Rigaku3014). The diffraction patterns of the finely powdered samples were obtained in a X–ray diffractometer using nickel filtered Cu–Ka radiation. Microstructure evaluation of the sintered products were observed by scanning electron microscope (SEM, Nova NanoSEM 230) using sputtered gold coating on the polished surface after thermal etching. The average grain size of sintered samples was determined on representative SEM micrographs using the linear intercept method by counting more than 200 grains [24].

The bending strength was measured on 5 bar samples (3 mm × 4 mm × 45 mm) in accordance with ASTM International standard C1161 [25]. The bending strength was measured using a CSS-44100 type universal tester with a loading rate of 0.5 mm/min. Bending strength (σ) was calculated from the following equation.

$$\sigma = \frac{3PL}{2bh^2} \quad (1)$$

where P, L, b and h represent maximum load of sample damage (N), the length of the support span (mm), width (mm) and thickness (mm), respectively.

Vickers hardness tests were carried out by the indentation method using Vickers hardness tester (450SVD, TMS, China). Indentation test was conducted on polished samples with a load of 2 kg held for 20 s. The length of each diagonal of the square shaped Vickers indentation was measured by optical microscope imaging. Vickers hardness (Hv) was calculated from the diagonal length of the indentation using the standard Vickers formula [26].

$$Hv = \frac{1.854P}{d^2} \quad (2)$$

where P is the applied indentation load and d is the mean value of the diagonal length of the indentation.

3. Results and discussion

3.1. Powder characterization

The XRD pattern of MAS powder calcined at 1200 °C is represented in Fig. 2. The mean crystallite size of the synthesized powder, calculated by Scherer equation, is 80 nm. The SEM micrograph of the MAS powder calcined at 1200 °C is shown in Fig. 3 and indicates that the synthesized powder has a mean particle size in the range 60–180 nm.

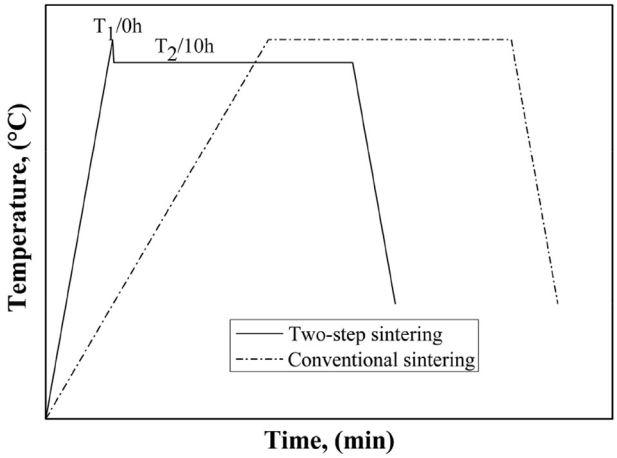

Fig. 1. Time–temperature profile of conventional sintering and two-step sintering.

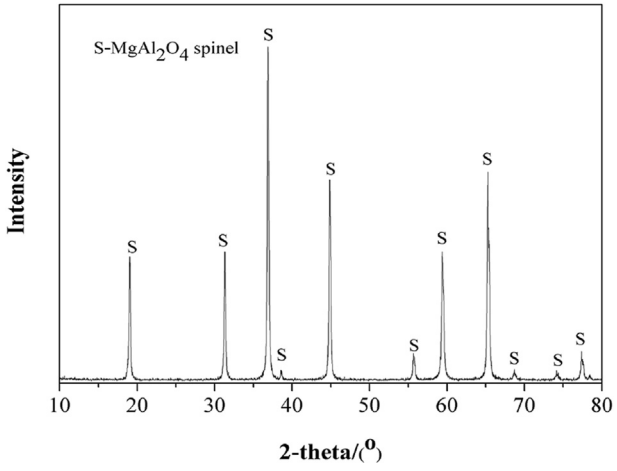

Fig. 2. XRD pattern of the MAS powder calcined at 1200 °C.