Rapid Synthesis and Consolidation of Nanostructured Mg_2SiO_4 - MgAl_2O_4 Composites

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Nanopowders of MgO , Al_2O_3 and SiO_2 were made by high energy ball milling. The rapid sintering of nanostructured MgAl_2O_4 - Mg_2SiO_4 composites was investigated by the pulsed current activated sintering process. The advantage of this process is that it allows very quick densification to near theoretical density and inhibition of grain growth. Highly dense nanostructured MgAl_2O_4 - Mg_2SiO_4 composites were produced with simultaneous application of 80 MPa pressure and pulsed current of 2800 A within 2 min. The sintering behavior, grain size and mechanical properties of MgAl_2O_4 - Mg_2SiO_4 composites were investigated. [doi:10.2320/matertrans.M2011188]

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1. Introduction

In recent years, some Si and Mg containing ceramics have drawn interests in the development of bone implant materials.¹⁻⁴⁾ Schwarz and Milne⁵⁾ have shown that silicon deficiency in rats result in skull deformation, with the cranial bones appearing flatter than normal. Magnesium is also undoubtedly one of the most important elements in human body, and closely associated with mineralization of calcined tissues and indirectly influences mineral metabolism.⁶⁾ Mg_2SiO_4 has been reported as a new machinable biomaterial, and might be used in dental and orthopedic prostheses.^{7,8)} Furthermore, Mg_2SiO_4 shows good refractoriness, with a melting point of 1890°C, low thermal expansion, good chemical stability, and excellent insulation properties even at high temperature.⁹⁾ However, the current concern about this material focuses on its low hardness and fracture toughness below the ductile-brittle transition temperature.^{10,11)} To improve their mechanical properties, the approach commonly utilized has been the addition of a second phase to form composites and to make nanostructured materials. One example is the addition of MgAl_2O_4 to Mg_2SiO_4 to improve the properties of the MgO . The attractive properties of MgAl_2O_4 are a high hardness (16 GPa), low density (3.58 g/cm³), high melting point (2135°C), high chemical inertness and high thermal shock resistance.¹²⁻¹⁴⁾

Nanocrystalline materials have received much attention as advanced engineering materials with improved physical and mechanical properties.^{15,16)} As nanomaterials possess high strength, high hardness, excellent ductility and toughness, undoubtedly, more attention has been paid for the application of nanomaterials.^{17,18)} In recent days, nanocrystalline powders have been developed by the thermochemical and thermomechanical process named as the spray conversion process (SCP), co-precipitation and high energy milling.¹⁹⁻²¹⁾ However, the grain size in sintered materials becomes much larger than that in pre-sintered powders due to a fast grain

growth during conventional sintering process. Therefore, even though the initial particle size is less than 100 nm, the grain size increases rapidly up to 2 μm or larger during the conventional sintering.²²⁾ So, controlling grain growth during sintering is one of the keys to the commercial success of nanostructured materials. In this regard, the pulsed current activated sintering method (PCASM) which can make dense materials within 2 min has been shown to be effective in achieving this goal.²³⁻²⁶⁾

In this work, we investigated the synthesis and sintering of MgAl_2O_4 - Mg_2SiO_4 composites by the PCAS method. The goal of this research is to produce dense nanostructured MgAl_2O_4 - Mg_2SiO_4 hard materials. In addition, we also studied the effect of MgAl_2O_4 on mechanical properties of MgAl_2O_4 - Mg_2SiO_4 composites.

2. Experimental Procedure

The Al_2O_3 powder with a grain size of <2.2 μm and 99.99% purity and amorphous SiO_2 powder with a grain size of <100 μm and 99.8% purity MgO powder with a grain size of <45 μm and 99% purity used in this research was supplied by Alfa. The powders (60 mol% MgO -20 mol% Al_2O_3 -20 mol% SiO_2) were first milled in a high-energy ball mill (Pulverisette-5 planetary mill) at 250 rpm for 4 h. Tungsten carbide balls (10 mm in diameter) were used in a sealed cylindrical stainless steel vial under an argon atmosphere. The weight ratio of balls-to-powder was 30 : 1.

The powders were placed in a graphite die (outside diameter, 45 mm; inside diameter, 20 mm; height, 40 mm) and then introduced into the Pulsed Current Activated Sintering (PCAS) apparatus shown schematically in reference.²³⁻²⁶⁾ The PCAS apparatus includes a 30 kW power supply which provides a pulsed current through the sample, and 50 kN uniaxial press. The system was first evacuated and a uniaxial pressure of 80 MPa was applied. A pulsed current was then activated and maintained until the densification rate was negligible, as indicated by real-time output of the shrinkage of the sample. The shrinkage was measured by a

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linear gauge measuring the vertical displacement. The PCAS can be controlled in two ways: by temperature control or by output control. The latter was chosen to investigate the effect of the output of total power, given that the pulsed current level has a direct effect on the rate of heating and on the maximum temperature. The output level was 90% output of total power. Temperatures were measured by a pyrometer focused on the surface of the graphite die. At the end of the process, the induced current was turned off and the sample cooled to room temperature. The process was carried out under a vacuum of 5.33 Pa.

The relative density of the sintered sample was measured by the Archimedes method. Microstructural information was obtained from product samples, which had been polished and etched using thermal etching for 1 h at 1000°C. Compositional and microstructural analyses of the products were made through X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) with energy dispersive spectroscopy (EDS). Vickers hardness was measured by performing indentations at a load of 5 kg and a dwell time of 15 s. The grain sizes of the Mg_2SiO_4 and MgAl_2O_4 was calculated from the full width at half-maximum (FWHM) of the diffraction peak by Suryanarayana and Grant Norton's formula.²⁷⁾

$$B_r \cos \theta = (B_{\text{crystalline}} + B_{\text{strain}}) \cos \theta = k\lambda/L + \eta \sin \theta \quad (1)$$

where B_r is FWHM of the diffraction peak after instrument correction; $B_{\text{crystalline}}$ and B_{strain} are FWHM caused by small grain size and internal stress, respectively; k is constant (with a value of 0.9); λ is wavelength of the X-ray radiation; L and η are grain size and internal strain, respectively; and θ is the Bragg angle. The parameters B and B_r follow Cauchy's form with the relationship: $B = B_r + B_s$, where B and B_s are FWHM of the broadened Bragg peaks and the standard sample's Bragg peaks, respectively.

3. Results and Discussion

Figure 1 shows X-ray diffraction patterns of the 60 mol%MgO-20 mol% Al_2O_3 -20 mol% SiO_2 powders after high-energy ball milling for 4 h. MgO and Al_2O_3 peaks are detected and SiO_2 peaks are not detected due to amorphous phase. From the result synthesis dose not occur during the milling.

FE-SEM images of 60 mol%MgO-20 mol% Al_2O_3 -20 mol% SiO_2 powders with milling for 4 h are shown in Fig. 2. MgO, Al_2O_3 and SiO_2 powders have round shape, refinement with milling and agglomeration. The variations of the shrinkage displacement and temperature with the heating time for 90% of the total output power capacity (30 kW) during the sintering of the high energy ball milled and unmilled 60 mol%MgO-20 mol% Al_2O_3 -20 mol% SiO_2 powders under a pressure of 80 MPa are shown in Fig. 3. The application of the pulsed current resulted in shrinkage due to consolidation. As pulsed current was applied, the shrinkage of high-energy ball milled powders gradually increased up to 900°C and then abruptly increased. While, the shrinkage of unmilled powders abruptly increased at about 1000°C. Figure 4 shows the XRD patterns of specimens heated to 900°C (a) and sintered to 1200°C (b), (c) from the high energy ball milled and unmilled 60 mol%MgO-20

Fig. 1 X-ray diffraction patterns of the milled 60 mol%MgO-20 mol% Al_2O_3 -20 mol% SiO_2 powder for 4 h.

Fig. 2 FE-SEM images of the milled 60 mol%MgO-20 mol% Al_2O_3 -20 mol% SiO_2 powders for 4 h.

mol% Al_2O_3 -20 mol% SiO_2 powders, respectively. X-ray diffraction results, shown in Fig. 4(a) exhibit only peaks pertaining to the reactants MgO and Al_2O_3 . However, when the temperature was raised to 1200°C, the starting powders reacted producing highly dense products of MgAl_2O_4 and Mg_2SiO_4 . The interaction between these phases, i.e.,

is thermodynamically feasible.²⁸⁾

The abrupt increase in the shrinkage displacement at the ignition temperature is due to the increase in density as a result of molar volume change associated with the formation of $\text{MgAl}_2\text{O}_4 + \text{Mg}_2\text{SiO}_4$ from $3\text{MgO} + \text{Al}_2\text{O}_3 + \text{SiO}_2$ reactant and the consolidation of the product. The combustion reaction temperature and the abrupt shrinkage initiation temperature decreased with milling time. The reasons are considered as follows. High-energy ball milling treatment allows the control of formation of compound by fixing the reactant powder microstructure. Indeed, high-energy ball milling produces finer crystallites, strain and defects. Therefore, consolidation temperature and combustion reaction temperature decrease with milling time because driving force

Fig. 3 Variations of temperature and shrinkage with heating time during the sintering of 60 mol%MgO-20 mol% Al_2O_3 -20 mol% SiO_2 powders milled for 4 h (a) and without milling (b).

Fig. 4 X-ray diffraction patterns of the specimens heated at 900°C (a) and sintered at 1200°C (b), (c) with milled powders and unmilled powders, respectively.

for sintering and contact points of the powders for atomic diffusion increases.

Plot of B_r ($B_{\text{crystalline}} + B_{\text{strain}}$) $\cos \theta$ versus $\sin \theta$ in Suryanarayana and Grant Norton's formula²⁷⁾ is shown in Fig. 5. The average grain sizes of the MgAl_2O_4 and Mg_2SiO_4 in $\text{MgAl}_2\text{O}_4 + \text{Mg}_2\text{SiO}_4$ composite sintered from milled powders calculated from the XRD data using Suryanarayana and Grant Norton's formula were about 60, 130 nm, respectively. Thus, the average grain size of the sintered MgAl_2O_4 and Mg_2SiO_4 are not greatly larger than that of the initial powder, indicating the absence of great grain growth during sintering. This retention of the grain size is attributed

Fig. 5 Plot of B_r ($B_{\text{crystalline}} + B_{\text{strain}}$) $\cos \theta$ versus $\sin \theta$ for (a) Mg_2SiO_4 and (b) MgAl_2O_4 in MgAl_2O_4 - Mg_2SiO_4 composite sintered milled powders.

to the high heating rate and the relatively short term exposure of the powders to the high temperature. FE-SEM images of $\text{MgAl}_2\text{O}_4 + \text{Mg}_2\text{SiO}_4$ composite sintered from 60 mol%MgO-20 mol% Al_2O_3 -20 mol% SiO_2 powders milled for 4 h are shown in Fig. 6. MgAl_2O_4 and Mg_2SiO_4 consist of nanocrystallines. In EDS, Al, Mg, Si and O peaks are detected and heavier contaminants, such as W and Fe from a ball or milling container, were not detected. The relative density of the product is about 99%.

The role of the current (resistive or inductive) in sintering and or synthesis has been focus of several attempts aimed at providing an explanation to the observed enhancement of sintering and the improved characteristics of the products. The role played by the current has been variously interpreted, the effect being explained in terms of fast heating rate due to Joule heating, the presence of plasma in pores separating powder particles,²⁹⁾ and the intrinsic contribution of the current to mass transport.³⁰⁻³²⁾

Vickers hardness measurements were performed on polished sections of the $\text{MgAl}_2\text{O}_4 + \text{Mg}_2\text{SiO}_4$ composite using a 5 kg load and 15 s dwell time. The Vickers hardnesses of $\text{MgAl}_2\text{O}_4 + \text{Mg}_2\text{SiO}_4$ composite sintered from 60 mol%MgO-20 mol% Al_2O_3 -20 mol% SiO_2 powders milled for 4 h was 1270 kg/mm², respectively. The hardnesses of $\text{MgAl}_2\text{O}_4 + \text{Mg}_2\text{SiO}_4$ composites increased with an addition of MgAl_2O_4 content.

Indentations with large enough loads produced median cracks around the indent. The length of these cracks permits the estimation of the fracture toughness of the materials by means of the expression:³³⁾

$$K_{IC} = 0.204(c/a)^{-3/2} \cdot H_v \cdot a^{1/2} \quad (3)$$

Fig. 6 FE-SEM image of MgAl_2O_4 - Mg_2SiO_4 composites sintered from milled powders.

Where c is the trace length of the crack measured from the center of the indentation, a is one half of the average length of the two indent diagonals, and H_v is the hardness. The calculated fracture toughness value for the MgAl_2O_4 + Mg_2SiO_4 composite sintered from 60 mol% MgO -20 mol% Al_2O_3 -20 mol% SiO_2 powders is about $3.2 \text{ MPa}\cdot\text{m}^{1/2}$, respectively. As in the case of the hardness value, the toughness value is the average of five measurements. The fracture toughness of MgAl_2O_4 + Mg_2SiO_4 composites is higher than monolithic Mg_2SiO_4 because of crack blocking of MgAl_2O_4 .¹¹⁾

4. Summary

Using the new rapid sintering method, PCAS, the densification of nanostructured MgAl_2O_4 - Mg_2SiO_4 composites was accomplished within 2 min from mechanically activated powders using high energy ball milling. The average grain sizes of the MgAl_2O_4 and Mg_2SiO_4 in MgAl_2O_4 - Mg_2SiO_4 composites were about 60, 130 nm, respectively. The Vickers hardness and fracture toughness of MgAl_2O_4 - Mg_2SiO_4 composites sintered from 60 mol% MgO -20 mol% Al_2O_3 -20 mol% SiO_2 powders milled for 4 h were 1270 kg/mm^2 and $3.2 \text{ MPa}\cdot\text{m}^{1/2}$, respectively. The hardness and fracture toughness of MgAl_2O_4 - Mg_2SiO_4 composites were higher than monolithic Mg_2SiO_4 .

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