Rapid Synthesis and Consolidation of Nanostructured Mg$_2$SiO$_4$-MgAl$_2$O$_4$ Composites

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Nanopowders of MgO, Al$_2$O$_3$ and Si$_2$O$_4$ were made by high energy ball milling. The rapid sintering of nanostructured MgAl$_2$O$_4$-Mg$_2$SiO$_4$ 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$_2$O$_4$-Mg$_2$SiO$_4$ 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$_2$O$_4$-Mg$_2$SiO$_4$ composites were investigated.

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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 Miline5) 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$_2$SiO$_4$ has been reported as a new machinable biomaterial, and might be used in dental and orthopedic prostheses.7,8) Furthermore, Mg$_2$SiO$_4$ 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$_2$O$_4$ to Mg$_2$SiO$_4$ to improve the properties of the MgO. The attractive properties of MgAl$_2$O$_4$ are a high hardness (16 GPa), low density (3.58 g/cm$^3$), high melting point (2135°C), high chemical inactivity 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 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$_2$O$_4$-Mg$_2$SiO$_4$ composites by the PCAS method. The goal of this research is to produce dense nanostructured MgAl$_2$O$_4$-Mg$_2$SiO$_4$ hard materials. In addition, we also studied the effect of MgAl$_2$O$_4$ on mechanical properties of MgAl$_2$O$_4$-Mg$_2$SiO$_4$ composites.

2. Experimental Procedure

The Al$_2$O$_3$ 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$_2$O$_3$-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. An 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$_2$SiO$_4$ and MgAl$_2$O$_4$ was calculated from the full width at half-maximum (FWHM) of the diffraction peak by Suryanarayana and Grant Norton’s formula.27)

\[ B_r \cos \theta = (B_{\text{crystalline}} + B_{\text{strain}}) \cos \theta = kL/L + \eta \sin \theta \quad (1) \]

where \( B_r \) is FWHM of the diffraction peak after instrument correction; \( B_{\text{crystalline}} \) and \( B_{\text{strain}} \) are FWHM caused by small grain size and internal stress, respectively; \( k \) is constant (with a value of 0.9); \( L \) is wavelength of the X-ray radiation; \( L \) and \( \eta \) are grain size and internal strain, respectively; and \( \theta \) 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 \( B_r \) 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$_2$O$_3$-20 mol% SiO$_2$ powders after high-energy ball milling for 4 h. MgO and Al$_2$O$_3$ 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$_2$O$_3$-20 mol% SiO$_2$ powders with milling for 4 h are shown in Fig. 2. MgO, Al$_2$O$_3$ 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$_2$O$_3$-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 displacement and temperature with the heating time decreased with milling time because driving force.

![X-ray diffraction patterns of the 60 mol% MgO-20 mol% Al$_2$O$_3$-20 mol% SiO$_2$ powder](image1)

![FE-SEM images of the milled 60 mol% MgO-20 mol% Al$_2$O$_3$-20 mol% SiO$_2$ powders](image2)
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 formula\(^{27}\) is shown in Fig. 5. The average grain sizes of the MgAl\(_2\)O\(_4\) and Mg\(_2\)SiO\(_4\) in MgAl\(_2\)O\(_4\) + Mg\(_2\)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\(_2\)O\(_4\) and Mg\(_2\)SiO\(_4\) 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 to the high heating rate and the relatively short term exposure of the powders to the high temperature. FE-SEM images of MgAl\(_2\)O\(_4\) + Mg\(_2\)SiO\(_4\) composite sintered from 60 mol%\(\text{MgO-20 mol%Al}_2\text{O}_3-20\text{ mol%SiO}_2\) powders milled for 4h are shown in Fig. 6. MgAl\(_2\)O\(_4\) and Mg\(_2\)SiO\(_4\) 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 MgAl\(_2\)O\(_4\) + Mg\(_2\)SiO\(_4\) composite using a 5 kg load and 15 s dwell time. The Vickers hardnesses of MgAl\(_2\)O\(_4\) + Mg\(_2\)SiO\(_4\) composite sintered from 60 mol%\(\text{MgO-20 mol%Al}_2\text{O}_3-20\text{ mol%SiO}_2\) powders milled for 4h was 1270 kg/mm\(^2\), respectively. The hardnesses of MgAl\(_2\)O\(_4\) + Mg\(_2\)SiO\(_4\) composites increased with an addition of MgAl\(_2\)O\(_4\) 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:\(^{33}\)

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

Fig. 3 Variations of temperature and shrinkage with heating time during the sintering of 60 mol%\(\text{MgO-20 mol%Al}_2\text{O}_3-20\text{ mol%SiO}_2\) 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.

Fig. 5 Plot of $B_r (B_{\text{crystalline}} + B_{\text{strain}}) \cos \theta$ versus $\sin \theta$ for (a) Mg\(_2\)SiO\(_4\) and (b) MgAl\(_2\)O\(_4\) in MgAl\(_2\)O\(_4\)-Mg\(_2\)SiO\(_4\) composite sintered milled powders.
The hardness and fracture toughness of MgAl$_2$O$_4$ composites were higher than monolithic Mg$_2$SiO$_4$. We are grateful for the financial support from the Korea Institute of Science and Technology, which was provided through the program for study on Development of Interfacial Engineering Technology Based Plasma.

REFERENCES


Fig. 6 FE-SEM image of MgAl$_2$O$_4$-Mg$_2$SiO$_4$ composites sintered from milled powders.