Pulsed Current Activated Synthesis and Consolidation of Nanostuctured MgTiO₃ Compound

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Nanopowders of MgO and TiO₂ were made by high energy ball milling. The rapid synthesis and sintering of nanostuctured MgTiO₃ compound 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 nanostuctured MgTiO₃ compound was 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 MgTiO₃ compound was investigated. [doi:10.2320/matertrans.M2012076]

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1. Introduction

The magnesium titanate (MgTiO₃) has been reported as ceramic capacitors and resonators because of its low dielectric loss and high thermal stability at high frequency.¹) Furthermore, the MgTiO₃ has a technological potential for applications in filters, antennas for communication, radar, direct broadcasting satellite and global positioning system operating at microwave frequencies.²,³)

Nanocrystalline materials have received much attention as advanced engineering materials with improved physical and mechanical properties.⁴,⁵) As nanomaterials possess high strength, high hardness, excellent ductility and toughness, undoubtedly, more attention has been paid for the application of nanomaterials.⁶,⁷) 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.⁸-¹⁰) 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.¹¹) So, controlling grain growth during sintering is one of the keys to the commercial success of nanomaterials. 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.¹²-¹⁶)

In this work, we investigated the synthesis and sintering of MgTiO₃ compound by the PCAS method. The goal of this research is to produce dense nanostructured MgTiO₃ material. In addition, we also studied on microstructure and mechanical properties of MgTiO₃ compound.

2. Experimental Procedure

The TiO₂ powder with a grain size of <45 µm and 99.8% purity and MgO powder with a grain size of <45 µm and 99% purity used in this research was supplied by Alfa. The powders (MgO–TiO₂) 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.¹²,¹³) The PCAS apparatus includes a 30 kW power supply which provides a pulsed current (on time; 20 µs and off time; 10 µs) 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 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 MgTiO3 was calculated from the full width at half-maximum (FWHM) of the diffraction peak by Suryanarayana and Grant Norton’s formula.17)

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

where \( B_r \) is the 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); \( \lambda \) 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 \( B_s \) 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 MgO–TiO2 powders after high-energy ball milling for 4 h. MgO and TiO2 peaks of reactant are detected and MgTiO3 peaks of product are not detected. From the result synthesis dose not occur during the milling. FE-SEM images of MgO and TiO2 powders with milling for 4 h are shown in Fig. 2. MgO and TiO2 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 MgO–TiO2 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 rapidly increased up to 1000°C and then was nearly constant. Figure 4 shows the XRD pattern of specimen heated to 1100°C from the high energy ball milled MgO–TiO2 powders. X-ray diffraction result exhibits only peaks pertaining to the product MgTiO3. The interaction between these phases, i.e.,
MgO + TiO₂ → MgTiO₃, \hspace{1cm} (2)

is thermodynamically feasible.\(^{18}\)

The abrupt increase in the shrinkage displacement in Fig. 3 is due to the increase in density as a result of molar volume change associated with the formation of MgTiO₃ from MgO + TiO₂ reactant and the consolidation of the product. 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 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 \(\sin \theta\) was shown in Fig. 5. The average grain sizes of the MgTiO₃ sintered from milled powders calculated from the XRD data using Suryanarayana and Grant Norton’s formula\(^{17}\) is about 70 nm. Thus, the average grain size of the sintered MgTiO₃ 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 MgTiO₃ consists of nanocrystallines. In EDS, Mg, Ti 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 heated to 900, 1000 and 1100°C is about 88, 98 and 99\%, respectively.

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,\(^{19}\) and the intrinsic contribution of the current to mass transport.\(^{20-22}\)

Vickers hardness measurements were performed on polished sections of the MgTiO₃ compound using a 5 kg load and 15 s dwell time. The Vickers hardness of MgTiO₃ compound sintered from MgO–TiO₂ powders milled for 4 h was 740 kg/mm². 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:\(^{23}\)

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

(3)

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 MgTiO₃ compound sintered from MgO–TiO₂ powders is about 2 MPa⋅m\(^{1/2}\). As in the case of the hardness value, the toughness value is the average of five measurements. The absence of reported values for hardness and toughness on MgTiO₃ compound precludes making direct comparison to the results obtained in this work to show the influence of grain size.

4. Summary

Nanopowders of MgO and TiO₂ were made by high energy ball milling. Using the new rapid sintering method, PCAS, the densification of nanostuctured MgTiO₃ compound was accomplished within 2 min from mechanically activated powders using high energy ball milling. The average grain size and relative density of the MgTiO₃ compound were about 70 nm and 99\%, respectively. The Vickers hardness and fracture toughness of MgTiO₃ compound sintered from MgO–TiO₂ powders milled for 4 h were 740 kg/mm² and 2 MPa⋅m\(^{1/2}\), respectively.
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