2015

In-situ formation and densification of MgAl2O4-SmAlO3 ceramics by a single-stage reaction sintering process

Beiyue Ma
Northeastern University

Yue Yin
Northeastern University China

Qiang Zhu
University of Wollongong, qiangz@uow.edu.au

Ying Li
Northeastern University

Guangqiang Li
Wuhan University of Science and Technology

See next page for additional authors

Publication Details
In-situ formation and densification of MgAl2O4-SmAlO3 ceramics by a single-stage reaction sintering process

Abstract
Stoichiometric magnesium aluminate spinel (MgAl2O4, MA)-samarium aluminate (SmAlO3, SA) ceramics have been prepared at 1580°C for 4h from calcined magnesia (MgO), commercial alumina (Al2O3) and samarium oxide (Sm2O3) by a single-stage in-situ reaction sintering (SIRS) method. The phase compositions, microstructures, shrinkage ratio, bulk density and cold compressive strength of the MA-SA ceramics have been investigated. The ceramics with 2.5 - 7.5 wt. % Sm2O3 are composed of MA and SA phases. The microstructures of the ceramics are dense. MA particles exist as angular shape, and their grain size varies between 2 and 10μm but the average grain size is about 5 μm. SmAlO3 particles form due to the reaction of Sm2O3 and Al2O3, and they distribute in the intergranular space of MA grains. The diameter shrinkage ratio, volume shrinkage ratio, bulk density and cold compressive strength of MA-SA ceramics are greatly improved due to the addition of Sm2O3.

Keywords
sintering, stage, process, formation, densification, situ, reaction, ceramics, single, smalo3, mgal2o4

Disciplines
Engineering | Science and Technology Studies

Publication Details

Authors
Beiyue Ma, Yue Yin, Qiang Zhu, Ying Li, Guangqiang Li, and Jingkun Yu

This journal article is available at Research Online: http://ro.uow.edu.au/eispapers/4629
IN-SITU FORMATION AND DENSIFICATION OF MgAl$_2$O$_4$–SmAlO$_3$ CERAMICS BY A SINGLE-STAGE REACTION SINTERING PROCESS

BEIYUE MA*, YUE YIN*, QIANG ZHU**, YING LI*, GUANGQIANG LI***, JINGKUN YU*

*School of Materials and Metallurgy, Northeastern University, Shenyang 110819, China
**School of Mechanical, Materials and Mechatronic Engineering, University of Wollongong, NSW 2522, Australia
***The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China

Keywords: MgAl$_2$O$_4$–SmAlO$_3$, Sm$_2$O$_3$, Reaction sintering, Sintering properties, Strength

Stoichiometric magnesium aluminate spinel (MgAl$_2$O$_4$, MA)–samarium aluminate (SmAlO$_3$, SA) ceramics have been prepared at 1580°C for 4 h from calcined magnesia (MgO), commercial alumina (Al$_2$O$_3$) and samarium oxide (Sm$_2$O$_3$) by a single-stage in-situ reaction sintering (SIRS) method. The phase compositions, microstructures, shrinkage ratio, bulk density and cold compressive strength of the MA–SA ceramics have been investigated. The ceramics with 2.5 - 7.5 wt. % Sm$_2$O$_3$ are composed of MA and SA phases. The microstructures of the ceramics are dense. MA particles exist as angular shape, and their grain size varies between 2 and 10 μm but the average grain size is about 5 μm. SmAlO$_3$ particles form due to the reaction of Sm$_2$O$_3$ and Al$_2$O$_3$, and they distribute in the intergranular space of MA grains. The diameter shrinkage ratio, volume shrinkage ratio, bulk density and cold compressive strength of MA–SA ceramics are greatly improved due to the addition of Sm$_2$O$_3$.

INTRODUCTION

Magnesium aluminate spinel (MgAl$_2$O$_4$, MA) has increasingly attracted much attention and been extensively used for refractory materials, optical ceramics and humidity sensors due to its excellent properties including high melting point (2135°C), high hardness (16.1 GPa), high flexural strength (180 MPa), low thermal expansion coefficient (~ 9 × 10$^{-6}$ °C$^{-1}$ between 30 and 1400°C), excellent transmittance in the range of 0.25 - 5.0 μm wavelength, good chemical inertness, thermal shock resistance and corrosion resistance [1-4]. A number of methods have been developed to fabricate MA ceramics such as reaction sintering [5], hot pressing sintering [6], high pressure sintering [7], microwave sintering [8] and spark plasma sintering [9], etc., among which reaction sintering is regarded as one of the most promising processes due to its simple operation and easy access of raw materials such as magnesite and bauxite [10] for example. MA ceramics with high density are very difficultly obtained by a single-stage reaction sintering process because the formation of spinel from oxides mixture usually companies a volume expansion of about 8% during the reaction [2]. To solve this problem, a two-stage reaction sintering process is often adopted: i) the formation of spinel is completed at a lower temperature at the first stage, and then ii) a sintering (or densification) process is conducted at the second stage. However, like other synthesis process mentioned above two-stage reaction sintering process suffers from expensive production cost and complexity.

An alternative way to improve the densification of MA during the sintering process is to introduce additives such as ZrO$_2$ [11], Cr$_2$O$_3$ [5], Dy$_2$O$_3$ [12], Nd$_2$O$_3$ [13] and AlCl$_3$ [14]. Moreover, some additives can also improve the mechanical properties and thermal shock resistance of MA ceramics. Ganesh et al. [11] found that yttria partially stabilized zirconia (YPSZ) additive increases the sintering ability, fracture toughness and hardness of MA materials. Sarkar et al. [5] reported that Cr$_2$O$_3$ additive has the greatest effect on the densification for alumina rich MA spinel at 1550°C, and 1.0 wt. % Cr$_2$O$_3$ addition is beneficial in restricting the strength degradation after thermal shock for the stoichiometric MA spinel. Tripathi et al. [12] found that Dy$_2$O$_3$ additive prevents the exaggerated grain growth and favors the densification of MA. Tian et al. [13] reported that Nd$_2$O$_3$ additive improves spinel crystallization and is beneficial to the sintering densification of MA. Ganesh et al. [14] reported that AlCl$_3$ is favorable for improving the formation and sintering densification of MA ceramics.

However, up to date, there are limited works published on the spinel formation and sintering densification of MA ceramics by addition of rare earths [12, 13],...
especially Sm$_2$O$_3$. In this paper, calcined MgO and commercial Al$_2$O$_3$ were used as raw materials, and Sm$_2$O$_3$ was chosen as the additive to prepare MA–SmAlO$_3$ (SA) ceramics, and the phase compositions, microstructures, shrinkage ratio, bulk density and cold compressive strength of the ceramics with 2.5 - 7.5 wt. % Sm$_2$O$_3$ additions have been investigated in detail.

EXPERIMENTAL

Preparation process

Table 1 lists raw materials for the synthesis of MA–SA ceramics. The powders of calcined MgO and commercial Al$_2$O$_3$ were weighted according to a MgO:Al$_2$O$_3$ mole ratio of 1:1. Sm$_2$O$_3$ was chosen as additive to form SmAlO$_3$ by an in-situ reaction between Sm$_2$O$_3$ and Al$_2$O$_3$, and its addition amounts were designed as 2.5, 5.0 and 7.5 wt. %. The powders containing above raw materials were fully milled for 3 h in a planetary ball mill with alcohol as the medium. The milled mixture powders were fully dried at 120°C, and then pressed at 200 MPa to form samples with dimension of 15 mm in diameter and 12 mm in height. All the formed samples were placed in a high temperature resistance furnace and sintered at 1580°C for 4 h.

Composition, microstructure and property characterization

The phase compositions of as-prepared MA–SA samples were characterized by X-ray diffraction (XRD, Cu Kα radiation, 30 kV and 30 mA). International Center for Diffraction Data (ICDD) cards used for identification were spinel (MA, 01–082–2424, 01–075–1797) and SmAlO$_3$ (00–052–1519, 00–029–0082). The microstructures and element distributions of as-prepared MA–SA samples were examined and scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS).

In this paper, sintering properties including diameter shrinkage ratio, volume shrinkage ratio and bulk density of MA–SA samples were studied. The diameter shrinkage ratio and volume shrinkage ratio of as-sintered samples (%) were calculated based on the Equations 1 and 2.

\[
\Delta D = \frac{D_0 - D_1}{D_0} \times 100\% \\
\Delta V = \frac{D_0^2H_0 - D_1^2H_1}{D_0^2H_0} \times 100\% 
\]

where $\Delta D$ and $\Delta V$ are the diameter shrinkage ratio and volume shrinkage ratio of as-sintered samples (%), $D_0$ is the bulk density of as-sintered samples (g·cm$^{-3}$), $D_0$ and $H_0$ are the diameter and height of the samples before sintering (mm), $D_1$ and $H_1$ are the diameter and height of the samples after sintering (mm), $m_1$ is the mass of a dried sample in air (g), $m_2$ is the mass of the sample in water (g), $m_3$ is the mass of the sample with free bubbles on the surface (g), and $d$ is the density of water (g·cm$^{-3}$).

The cold compressive strength of MA-SA samples was measured using a CMT5105 type universal tester with loading rate of 0.5 mm·min$^{-1}$. The sample size was φ 15 mm × 12 mm. The cold compressive strength (CS) was calculated by Equation 4.

\[
CS = \frac{P}{A}
\]

where $CS$, $P$ and $A$ represent the cold compressive strength (MPa), maximum load of sample damage (N) and sample compressive area (mm$^2$), respectively.

RESULTS AND DISCUSSION

Phase compositions

Figure 1 shows XRD diffraction patterns of as-synthesized MA–SA ceramics at 1580°C for 4 h. The XRD analysis shows that MgO and Al$_2$O$_3$ phases can not be detected after sintering, which means that MgO fully reacted with Al$_2$O$_3$ and completely formed MgAl$_2$O$_4$. It was also found that a new phase SmAlO$_3$ formed, which indicates that there was a chemical reaction occurring between Sm$_2$O$_3$ and Al$_2$O$_3$ during the sintering process. With increasing amounts of Sm$_2$O$_3$ additive from 2.5 up

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Chemical compositions (wt. %)</th>
<th>Particle size (μm)</th>
<th>Production place</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcined MgO</td>
<td>99</td>
<td>74</td>
<td>Liaoning Yingkou Qinghua Group Co. Ltd., China</td>
</tr>
<tr>
<td>Commercial Al$_2$O$_3$</td>
<td>–</td>
<td>44</td>
<td>Henan Xingyang Tenai Grinding Materials Co. Ltd., China</td>
</tr>
<tr>
<td>Chemical reagent Sm$_2$O$_3$</td>
<td>–</td>
<td>–</td>
<td>Sinopharm Chemical Reagent Co. Ltd, China</td>
</tr>
</tbody>
</table>
to 7.5 wt. %, the diffraction intensity of SmAlO₃ increases (Figure 1a-c). Based on the Al₂O₃-Sm₂O₃-ZrO₂ phase diagram, the SmAlO₃ and Sm₄Al₂O₉ compounds are formed at 1250 and 1650°C [17]. In this study, the Sm₄Al₂O₉ compound can not be produced due to small amount of Sm₂O₃ additive (2.5 - 7.5 wt. %) in sample.

The reactions of MgO and Sm₂O₃ with Al₂O₃ to synthesize MgAl₂O₄ and SmAlO₃ are shown in Equations 5 and 6. The expression between standard Gibbs free energy (ΔG°) and temperature (T, K) of reaction (5) is as below [18].

\[
\begin{align*}
\text{MgO(s)} + \text{Al}_2\text{O}_3(s) &= \text{MgAl}_2\text{O}_4(s) \quad (5) \\
\text{Sm}_2\text{O}_3(s) + \text{Al}_2\text{O}_3(s) &= \text{SmAlO}_3(s) \quad (6)
\end{align*}
\]

\[
\Delta G^\circ (J\cdot mol^{-1}) = -35 600 - 2.09T (K) \quad (7)
\]

In this study, sintering temperature was set as 1580°C (T = 1853 K), therefore \(\Delta G^\circ\) is calculated as -39 472.77 J·mol⁻¹. It reveals that the thermodynamic requirement for producing MgAl₂O₄ from MgO and Al₂O₃ is fully satisfied.

Microstructures and elements distributions

Figure 2 shows SEM images of as-prepared MA-SA ceramics at 1580°C for 4 h. It can be seen that there is no obvious porosity existing in the microstructure of MA-SA ceramics. It was observed that there exist gray and big particles as well as white and small particles or cotton-like material. The gray and big particles have an angular shape, and their grain size varies between 2 and 10 μm but the average grain size is about 5 μm. The average grain size of white and small particles is about 2 μm.

Figure 3 shows EDS spectrums of MA-SA ceramics doped with 2.5 – 7.5 wt. % Sm₂O₃ and sintered at 1580°C for 4 h. EDS analysis shown in Figure 3a indicates that white and small particle (zone A) consists of Al, Mg, O and Sm elements, and gray and big particle (zone A') is composed of Al, Mg and O elements. Combining with XRD patterns shown in Figure 1, zone A and A' are SmAlO₃ and MgAl₂O₄, respectively. It can be seen from Figure 3b that cotton-like material (zone B) is mainly composed of Al, Mg, O and Sm elements, and zone B is SmAlO₃. In Figure 3c white particle C mainly consists of Al, O and Sm elements, and zone C is SmAlO₃.
It is important noted that Mg shown in Figure 3a and b possibly derives from the MA matrix element. During the EDS analysis, the spot size of electron beam is quite large, probably greater than 1 μm in dimension, it is rather like a small area analysis than a spot. When the particle shown in Figure 3a and b is too small, the surrounding matrix will lead to the detection of Mg element. Thus, zones A and B are concluded be SmAlO₃. Moreover, Ca and Si elements shown in Figure 3b are possibly from raw materials, Au and Pd shown in Figure 3c can be observed due to the metal coating of the samples used for SEM characterization.

It can also be observed from Figure 2 that the formed SmAlO₃ particles are mainly present in the intergranular space and grain boundaries of MA particles.

Figure 3. EDS spectrums of zones A, A’, B and C shown in Figure 2: a) zone A, a’) zone A’, b) zone B and c) zone C.

Sintering properties and cold compressive strength

Figure 4 shows diameter shrinkage ratio and volume shrinkage ratio of MA–SA ceramics doped with 2.5 - 7.5 wt. % Sm₂O₃ and sintered at 1580°C for 4 h. It is clearly observed that MA–SA samples with 2.5 - 7.5 wt. % Sm₂O₃ additions have high shrinkage ratios. With increasing the additive amount of Sm₂O₃, the diameter shrinkage ratio and volume shrinkage ratio of the samples gradually increase. The diameter shrinkage ratio and volume shrinkage ratio of the sample added with 2.5 wt. % Sm₂O₃ are 10.57 % and 28.17 %, respectively. For the sample by addition of 5.0 wt. % Sm₂O₃, its diameter shrinkage ratio and volume shrinkage ratio
increase to 11.12 % and 29.10 %, respectively. When 7.5 wt. % Sm$_2$O$_3$ was doped, the diameter shrinkage ratio and volume shrinkage ratio achieve their maximum values of 11.25 % and 29.76 %, respectively.

Figure 5 shows change curves of bulk density and cold compressive strength of MA–SA ceramics doped with various amounts of Sm$_2$O$_3$ and sintered at 1580°C for 4 h. It was clearly found that the MA–SA samples with 2.5 – 7.5 wt. % Sm$_2$O$_3$ additions have high bulk density and cold compressive strength. With increasing addition amounts of Sm$_2$O$_3$ ranging from 2.5 wt. % to 5.0 wt. %, the bulk density gradually increases from 3.07 to 3.12 g·cm$^{-3}$, and the strength increases from 197.9 to 198.9 MPa. The sample doped with 7.5 wt. % Sm$_2$O$_3$ gets its maximum density of 3.13 g·cm$^{-3}$, and has maximum strength of 209.4 MPa. To some extent the formed SmAlO$_3$ particles occupy the grain boundary position (Figure 2), inhibit the grain growth of MA, and they can further improve the density of MA ceramics [12]. The in-situ formed SmAlO$_3$ from Sm$_2$O$_3$ and Al$_2$O$_3$ partly contributes to the increase of cold compressive strength of MA–SA ceramics. Additional detailed research and characterization need to be performed to fully understand the reason on how to increase the strength due to the addition of Sm$_2$O$_3$. It is concluded from Figures 4 and 5 that Sm$_2$O$_3$ additive favors to improve the diameter shrinkage ratio, volume shrinkage ratio, bulk density and cold compressive strength of MA–SA ceramics.

CONCLUSIONS

- Dense MgAl$_2$O$_4$–SmAlO$_3$ ceramics have been successfully prepared at 1580°C for 4 h by the single-step in-situ reaction sintering method.
- MgAl$_2$O$_4$ and SmAlO$_3$ are formed due to the reactions of MgO and Al$_2$O$_3$ as well as Sm$_2$O$_3$ and Al$_2$O$_3$. MgAl$_2$O$_4$ particles have an angular shape, and their grain size varies between 2 and 10 μm but the average grain size is about 5 μm. SmAlO$_3$ particles form due to the reaction of Sm$_2$O$_3$ and Al$_2$O$_3$, and they distribute in the intergranular space of MA grains.
- With increasing the addition amounts of Sm$_2$O$_3$, the sintering properties and post-sintering properties of MgAl$_2$O$_4$–SmAlO$_3$ ceramics all improve gradually. The MgAl$_2$O$_4$–SmAlO$_3$ ceramics with 7.5 wt. % Sm$_2$O$_3$ addition achieve their maximum diameter shrinkage ratio, volume shrinkage ratio, bulk density and cold compressive strength, 11.25 %, 29.76 %, 3.13 g·cm$^{-3}$ and 209.4 MPa, respectively.

Acknowledgments

The authors gratefully acknowledge the support of the open research fund for the State Key Laboratory of Refractories and Metallurgy of WUST (Grant No. G201402), the Fundamental Research Funds for the Central Universities (Grant No. N120402006) and National Natural Science Foundation of China (Grant No. 51474057).

REFERENCES