EFFECTS OF NANO-ZrO₂ ADDITIVE ON THE PHASE TRANSFORMATION AND DENSIFICATION OF ZrO₂–MgAl₂O₄ CERAMICS PREPARED BY SINGLE-STAGE SRS PROCESS


*School of Metallurgy, Northeastern University, Shenyang 110819, PR China
**The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, PR China
***Electron Microscope Unit, Mark Wainwright Analytical Centre, The University of New South Wales, Sydney, NSW 2032, Australia

#E-mail: maby@smm.neu.edu.cn

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A series of ZrO₂–MgAl₂O₄ ceramics with additions of 0; 2.5; 5.0; and 7.5 wt. % nano-ZrO₂ were successfully fabricated at 1580°C for 4 h from powders of commercial Al₂O₃ and calcined MgO by single-stage solid state reaction sintering (SRS) method. Effects of nano-ZrO₂ additive on the phase compositions, microstructures and bulk density of the ceramics were investigated. Nano-ZrO₂ additive was found to remarkably promote the sintering densification and improve the microstructure of the ceramics. Uniform, dense and fine microstructures are obtained, and the mean grain size of MgAl₂O₄ particles is about 2 μm. The as-prepared ceramics mainly consist of MgAl₂O₄ and c-ZrO₂ (cubic-Ca₀.₁₅Zr₀.₈₅O₁.₈₅), due to the reaction between Al₂O₃ and MgO as well as the nano-ZrO₂ additive and CaO stabilizer. The formation process of the ceramics mainly includes the synthesis of MgAl₂O₄ and the conversion process of m-ZrO₂ to c-ZrO₂ under the stabilizing action of CaO.

INTRODUCTION

Magnesium aluminate spinel (MgAl₂O₄) has been attracted much attention due to its excellent properties such as high melting point, high strength, high hardness, low thermal expansion coefficient, good chemical inertness, good wear resistance and thermal shock resistance, and has been widely used in many fields including metallurgy, cement, glass and ceramic industries [1, 2].

With the development of above industrial technologies, MgAl₂O₄ based ceramics have received a great deal attention to meet the demand of high temperature service environment. Numerous preparation methods have been developed, such as reaction sintering [3], spark plasma sintering [4], hot pressing sintering [5], microwave sintering [6], and molten salt method [7], etc., among which reaction sintering is regarded as one of the most promising and popular process due to its simple operation and easy access of raw materials such as magnesite and bauxite [8] for example. MgAl₂O₄ ceramic with high density are very difficult 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 [9]. A two-stage reaction sintering process is often adopted in order to solve this problem. The formation of spinel is completed at a lower temperature at the first stage, and then 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.

To prepare the dense MgAl₂O₄ based ceramics, some oxide additives such as ZrSiO₄ [10-12], TiO₂ [13], SiO₂ [13], CaCO₃ [13], Cr₂O₃ [14], Dy₂O₃ [15], Sm₂O₃ [16], Y₂O₃ and Nb₂O₅ [17] have been chosen, and the spinel formation, densification, microstructure, etc., were found to be remarkably improved. Addition of ZrSiO₄-3 mol. % Y₂O₃ reduced the size of MgO grains, improved the bulk density, fracture toughness and thermal stress parameters of MgO–MgAl₂O₄ ceramics [10]. SiO₂ and CaCO₃ additives enhanced the densification of MgAl₂O₄ ceramic due to the formation of glassy phases in grain boundary region, and addition of TiO₂ remarkably improved the densification of the ceramic because of the formation of TiAl₂O₅ in grain boundaries and inside grains [13]. Cr₂O₃ additive was found to restrict the strength degradation after thermal shock for the stoichiometric MgAl₂O₄ ceramic [14]. Dy₂O₃ additive prevented the exaggerated grain growth and benefited to the sintering densification of MgAl₂O₄ ceramic [15]. Additions of Sm₂O₃ [16], Y₂O₃ and Nb₂O₅ [17] were reported to effectively improve the densification and cold compressive strength of MgAl₂O₄ ceramic in our previous work.
So far, to our knowledge, there are few reports on the improvement of sintering densification and microstructure of ZrO$_2$–MgAl$_2$O$_4$ ceramics by addition of ZrO$_2$ [18-20], especially nano-ZrO$_2$. In this study, a series of ZrO$_2$–MgAl$_2$O$_4$ ceramics doped with various amounts of nano-ZrO$_2$ were fabricated from commercial Al$_2$O$_3$ and calcined MgO by the single-stage SRS method. Effects of nano-ZrO$_2$ additive on the phase compositions, microstructures and densification behavior of ZrO$_2$–MgAl$_2$O$_4$ ceramics were investigated. The preparation process of the ceramics was also discussed.

**EXPERIMENTAL**

**Materials**

Table 1 lists the raw materials used for the fabrication of ZrO$_2$–MgAl$_2$O$_4$ ceramics in this study.

**Preparation of sample**

The chemical reaction of MgAl$_2$O$_4$ from Al$_2$O$_3$ and MgO is shown in Equation 1.

$$\text{Al}_2\text{O}_3(s) + \text{MgO}(s) = \text{MgAl}_2\text{O}_4(s)$$

In order to prepare stoichiometric MgAl$_2$O$_4$, commercial Al$_2$O$_3$ and calcined MgO powders was weighted according to a molar ratio of 1:1. Nano-ZrO$_2$ was chosen as additive and its addition amounts were designed as 0; 2.5; 5.0 and 7.5 wt. %, which were marked as Z0, Z1, Z2 and Z3, respectively. CaO was used as a stabilizer for monoclinic phase ZrO$_2$ (m-ZrO$_2$) to form CaO partially stabilized ZrO$_2$, namely cubic phase (c-ZrO$_2$) in as-sintered ZrO$_2$–MgAl$_2$O$_4$ ceramics, and the addition amount of CaO stabilizer was calculated according to $n\text{CaO}:n(\text{CaO}+\text{ZrO}_2) = 60$ mol. %. The powders containing above raw materials and additives were milled for 3 h in a planetary ball mill with alcohol as a medium. The as-milled powders were fully dried at 120°C, and they were pressed at 200 MPa to form a series of samples with size of $\phi$ 15 mm $\times$ 12 mm. Finally, the as-formed samples were all sintered at 1580°C for 4 h in air. The specific sintered system is as follows: the samples were heated from room temperature to 1000°C through a rate of 8°C·min$^{-1}$, and further heated to 1300°C through a rate of 5°C·min$^{-1}$, followed by a rate of 3°C·min$^{-1}$ to 1580°C and held for 4 h, and then cooled to 1000°C through a rate of 10°C·min$^{-1}$, and finally the samples were air-cooled to room temperature.

**Characterization of sample**

ZrO$_2$–MgAl$_2$O$_4$ ceramic samples were taken out after cooling at room temperature. The surface of samples was polished, and scanning electronic microscope attached with energy dispersive spectrometry (SEM-EDS) was used to observe the microstructures and to measure micro area compositions of samples. Meanwhile, X-ray diffraction (XRD) was employed to examine the phase compositions of samples. The bulk densities of the samples with addition of various amounts of nano-ZrO$_2$ were measured in water under vacuum using Archimedes’ principle and calculated by Equation 2 [21].

$$D_b = \frac{m_1 d}{m_3 - m_2}$$

where $D_b$ is the bulk density of as-sintered samples (g·cm$^{-3}$), $m_1$ 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 (1.0 g·cm$^{-3}$).

**RESULTS AND DISCUSSION**

**Phase transformation**

Figure 1 shows XRD patterns of as-prepared ZrO$_2$–MgAl$_2$O$_4$ ceramic samples doped with 0; 2.5; 5.0 and 7.5 wt. % nano-ZrO$_2$, and sintered at 1580°C for 4 h. It was clearly found that ZrO$_2$ additive has a great influence on the phase compositions of as-synthesized ZrO$_2$–MgAl$_2$O$_4$ samples. For the undoped sample Z0, MgAl$_2$O$_4$ is formed, and Al$_2$O$_3$ and MgO phases are not
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detected. It reveals that during the sintering process, the chemical reaction between Al$_2$O$_3$ and MgO completely occurs at 1580°C for 4 h. Besides MgAl$_2$O$_4$, CaO·Al$_2$O$_3$ is also detected, and it is a reactive product of CaO and Al$_2$O$_3$, and its peak intensity is very low. When 2.5 wt. % nano-ZrO$_2$ was added, great changes in the phase compositions of sample Z1 happens. A new phase, c-ZrO$_2$ (Ca$_{0.15}$Zr$_{0.85}$O$_{1.85}$), which is a solid solution between ZrO$_2$ and CaO stabilizer, is observed in sample Z1. It can be seen that the peak intensity of c-ZrO$_2$ in sample Z2 (5.0 wt. % nano-ZrO$_2$) increases. The main crystalline phases of samples Z1 and Z2 all are c-ZrO$_2$ and MgAl$_2$O$_4$. In the sample Z3 with addition of 7.5 wt. % nano-ZrO$_2$, a new phase, m-ZrO$_2$, is formed. It shows that a small amount of nano-ZrO$_2$ cannot form the ZrO$_2$–CaO solid solution due to the lack of CaO stabilizer in sample, and the peak intensity of m-ZrO$_2$ is also very weak. Hence, ZrO$_2$–MgAl$_2$O$_4$ ceramics containing c-ZrO$_2$ can be successfully fabricated at 1580°C for 4 h from the powders of Al$_2$O$_3$, MgO, CaO and nano-ZrO$_2$ by the single-stage SRS method.

Figure 1. XRD patterns of as-prepared ZrO$_2$–MgAl$_2$O$_4$ ceramic samples doped with various amounts of nano-ZrO$_2$ and sintered at 1580°C for 4 h.

Figure 2. SEM images of as-prepared ZrO$_2$–MgAl$_2$O$_4$ ceramic samples doped with: a) 0 wt. %, b) 2.5 wt. %, c) 5.0 wt. % and d) 7.5 wt. % nano-ZrO$_2$ and sintered at 1580°C for 4 h.
Microstructures

Figure 2 shows SEM images of as-prepared ZrO$_2$–MgAl$_2$O$_4$ ceramic samples doped with 0; 2.5; 5.0 and 7.5 wt. % nano-ZrO$_2$ and sintered at 1580°C for 4 h. Nano-ZrO$_2$ additive was found to remarkably improve the microstructures of the ceramics. For the undoped sample Z0 (Figure 2a), MgAl$_2$O$_4$ particles exist as granular shape. Their mean particle size is about 5 μm, and their grain sizes range from 1 to 10 μm. When 2.5 wt. % ZrO$_2$ was doped (Figure 2b), uniform and compact microstructure of sample Z1 is formed. The mean grain size of...
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MgAl2O4 particles is dramatically decreased to about 2 μm, and they exist as prismatic shape. It attributes to the introduction of the nano-ZrO2. When the doping amount of nano-ZrO2 was further increased to 5.0 wt. % and 7.5 wt. % (Figures 2c, d), respectively, the micro-structures of samples Z2 and Z3 are all improved compared with that of the sample Z0. Thus, nano-ZrO2 additive is favorable for improving the microstructures of ZrO2–MgAl2O4 ceramics.

Figure 3 shows back-scattering photos and EDS spectrums of as-synthesized ceramics doped with 0 and 5.0 wt. % nano-ZrO2 respectively and sintered at 1580°C for 4 h. A large numbers of dark gray particles in the undoped sample Z0 consist of Al, Mg, O and Ca elements. Combining with XRD patterns shown in Figure 1, these gray particles are concluded as MgAl2O4–CaAl2O4 composite body (Figure 3a). The observed gray and big particles in sample Z2 are composed of Al, Mg, O, Ca and Zr elements, and they are MgAl2O4Ca0.15Zr0.85O1.85 composite body (Figure 3b). Moreover, white and small particles are c-ZrO2 (Ca0.15Zr0.85O1.85) (Figure 3c), and dark gray and small particles are MgAl2O4 (Figure 3d).

**Bulk density**

Figure 4 shows the effect of nano-ZrO2 additive on the bulk density of as-prepared ZrO2–MgAl2O4 ceramic samples sintered at 1580°C for 4 h. It is clearly observed that adding ZrO2 greatly affects the bulk density of samples. With increasing the addition amount of ZrO2, the bulk density increases gradually. The bulk density of undoped sample Z0 is 3.15 g·cm\(^{-3}\). When 2.5 wt. % ZrO2 was added (sample Z1), the bulk density sharply increases to 3.20 g·cm\(^{-3}\). Further increase of ZrO2 addition amount to 5.0 wt. % (sample Z2) and 7.5 wt. % (sample Z3), the bulk densities steadily increases to 3.22 and 3.23 g·cm\(^{-3}\), respectively.

**Figure 4.** Effect of addition amounts of nano-ZrO2 on the bulk density of as-prepared ZrO2–MgAl2O4 ceramic samples sintered at 1580°C for 4 h.

During the sintering process of MgO–MgAl2O4 ceramics containing ZrO2 additive, Zr\(^{4+}\) goes into MgO lattice to form a ZrO2–MgO solid solution, which creates mag-nesium ion vacancies in MgO crystals, and then the formed vacancies accelerate the oxygen ion diffusion to produce dense spinel products at over 1500°C [18]. Another study also indicated that ZrO2 additive can improve the sinterability of MgAl2O4 by accelerating the oxygen ion diffusion [22]. In this study, the density is increased due to the addition of nano-ZrO2 (Figure 4). Moreover, when nano-ZrO2 was added to the MgAl2O4 based ceramics, nano-ZrO2 grains mostly exist at grain boundaries of MgAl2O4 particles (Figure 3), which controls grain growth, accelerates the oxygen ion diffusion through the grain boundaries, and thus promotes the sintering process [18].

**Thermodynamic analysis of formation process**

During the preparation process of ZrO2–MgAl2O4 ceramics, the following chemical reactions maybe occur. Main reactions for producing ZrO2–MgAl2O4 ceramics are shown in Equations 3 and 4. The relationship expressions between standard Gibbs free energy (\(\Delta G^\theta\), J·mol\(^{-1}\)) and temperature (\(T\), K) are as follows [23, 24].

\[
\begin{align*}
\text{CaO} (s) + \text{ZrO}_2 (s) &= \text{CaO}·\text{ZrO}_2 (s) \quad (4') \\
\end{align*}
\]

\[
\begin{align*}
\Delta G^\theta_{4'} / J \cdot mol^{-1} &= -12 600 - 24.69 T(K) \\
\Delta G^\theta_{4'} / J \cdot mol^{-1} &= -16 380 - 37.58 T(K) \\
\Delta G^\theta_{4'} / J \cdot mol^{-1} &= -16 700 - 25.52 T(K) \\
\Delta G^\theta_{4'} / J \cdot mol^{-1} &= -18 000 - 18.83 T(K) \\
\Delta G^\theta_{4'} / J \cdot mol^{-1} &= -18 380 - 16.83 T(K) \\
\end{align*}
\]

Figure 5 shows \(\Delta G^\theta\)–\(T\) curve for Al2O3–MgO–CaO–ZrO2 system plotted according to reactions 3–8 and their relationship expressions between \(\Delta G^\theta\) and \(T\). In this study, the experimental temperature is 1 580°C (1853 K), so the \(\Delta G^\theta\) values at 1 853 K (dash line in Figure 5) ordered by size are \(\Delta G^\theta_8 < \Delta G^\theta_7 < \Delta G^\theta_6 < \Delta G^\theta_5 < \Delta G^\theta_4\), and they are all negative. It reveals that reaction 8 easily occurs according to the relational...
thermodynamic. However, reaction 3 is the most difficult to generate. It is important noted that reaction 4 is replaced by reaction 4’ due to the lack of thermodynamic data of reaction 4. Moreover, the $\Delta G^\theta$ value of $T > 1\,808\,\text{K}$ cannot be calculated due to the thermodynamic expression is used in $T$ between 773 and 1 808 K, so the curve of reaction 5 at $T > 1\,808\,\text{K}$ is plotted as dotted line.

- The as-prepared ZrO$_2$-MgAl$_2$O$_4$ ceramics mainly include MgAl$_2$O$_4$ and c-ZrO$_2$ (cubic-Ca$_{0.15}$Zr$_{0.85}$O$_{1.85}$) phases. The mean grain size of MgAl$_2$O$_4$ particles is about 2 μm.
- The formation process of ZrO$_2$-MgAl$_2$O$_4$ ceramics includes the production of MgAl$_2$O$_4$, and the conversion of m-ZrO$_2$ to c-ZrO$_2$ under the stabilizing action of CaO.

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## CONCLUSIONS

- A stoichiometric MgAl$_2$O$_4$ spinel with a bulk density of 3.15 g cm$^{-3}$ can be prepared following a single-stage SRS process at 1 580°C for 4 h from a powder mixture of commercial Al$_2$O$_3$ and calcined MgO.
- The introduction of nano-ZrO$_2$ can remarkably promote the sintering densification of ZrO$_2$-MgAl$_2$O$_4$ ceramics and improve the microstructures, and dense ceramics with bulk density of 3.23 g cm$^{-3}$ were successfully prepared when sintered at 1 580°C for 4 h.
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