

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

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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-Ca_{0.15}Zr_{0.85}O_{1.83}), 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 accompanies 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 forma-

tion 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 $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ ceramics by addition of ZrO_2 [18-20], especially nano- ZrO_2 . In this study, a series of $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ ceramics doped with various amounts of nano- ZrO_2 were fabricated from commercial Al_2O_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 $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ ceramics were investigated. The preparation process of the ceramics was also discussed.

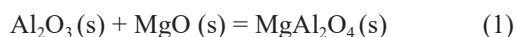
EXPERIMENTAL

Materials

Table 1 lists the raw materials used for the fabrication of $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ ceramics in this study.

Preparation of sample

The chemical reaction of MgAl_2O_4 from Al_2O_3 and MgO is shown in Equation 1.



In order to prepare stoichiometric MgAl_2O_4 , commercial Al_2O_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 $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ 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 $\phi 15 \text{ mm} \times 12 \text{ mm}$. 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 $8^\circ\text{C}\cdot\text{min}^{-1}$, and further heated to 1300°C through a rate of $5^\circ\text{C}\cdot\text{min}^{-1}$, followed by a rate of $3^\circ\text{C}\cdot\text{min}^{-1}$ to 1580°C and held for 4 h, and then cooled to 1000°C through a rate of $10^\circ\text{C}\cdot\text{min}^{-1}$, and finally the samples were air-cooled to room temperature.

Characterization of sample

$\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ 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].

$$D_b = \frac{m_1 d}{m_3 - m_2} \quad (2)$$

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

RESULTS AND DISCUSSION

Phase transformation

Figure 1 shows XRD patterns of as-prepared $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ 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 $\text{ZrO}_2\text{-MgAl}_2\text{O}_4$ samples. For the undoped sample Z0, MgAl_2O_4 is formed, and Al_2O_3 and MgO phases are not

Table 1. Chemical compositions and mean particle size of raw materials.

Raw materials	Commercial Al_2O_3	Calcined MgO	Chemical reagent CaO	Chemical reagent nano- ZrO_2
Al_2O_3	98.66	0.26	—	—
MgO	—	95.32	—	—
Chemical CaO	—	1.10	99.99	—
composi- ZrO_2	—	—	—	99.99
tions SiO_2	0.02	2.89	—	—
(wt. %) Fe_2O_3	0.02	0.43	—	—
Na_2O	0.30	—	—	—
Loss of ignition	1.00	—	—	—
Mean particle size (μm)	≤ 44	≤ 74	44	0.05

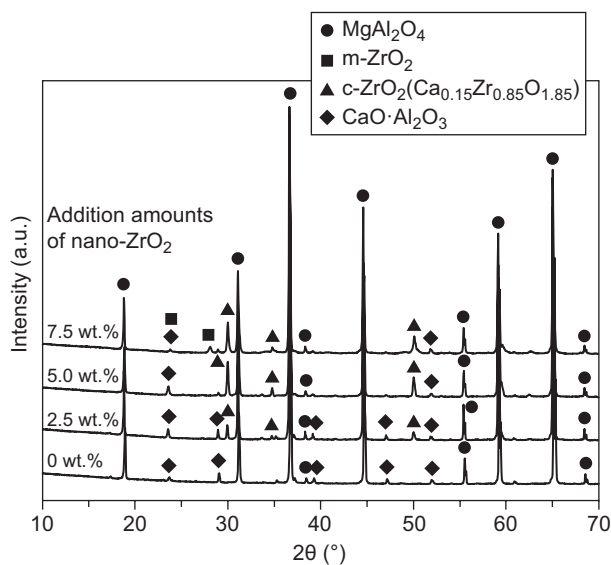
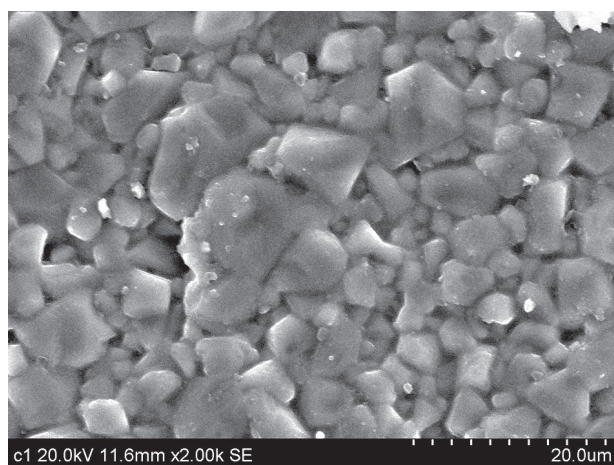
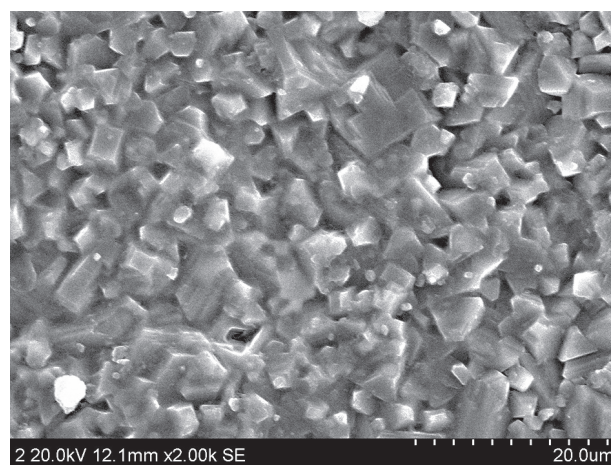


Figure 1. XRD patterns of as-prepared ZrO₂-MgAl₂O₄ ceramic samples doped with various amounts of nano-ZrO₂ and sintered at 1580°C for 4 h.

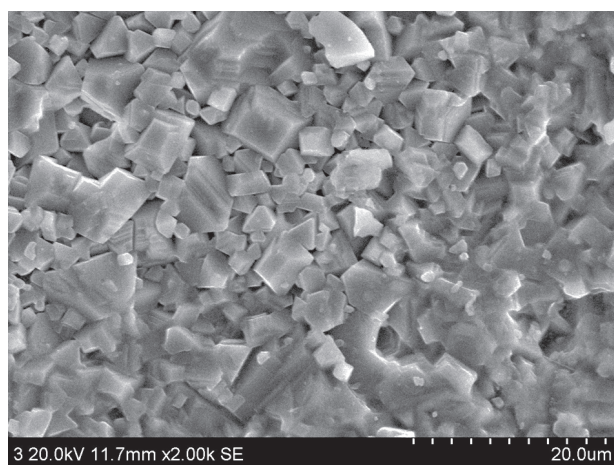
detected. It reveals that during the sintering process, the chemical reaction between Al₂O₃ and MgO completely occurs at 1580°C for 4 h. Besides MgAl₂O₄, CaO·Al₂O₃ is also detected, and it is a reactive product of CaO and Al₂O₃, and its peak intensity is very low. When 2.5 wt. % nano-ZrO₂ was added, great changes in the phase compositions of sample Z1 happens. A new phase, c-ZrO₂ (Ca_{0.15}Zr_{0.85}O_{1.85}), which is a solid solution between ZrO₂ and CaO stabilizer, is observed in sample Z1. It can be seen that the peak intensity of c-ZrO₂ in sample Z2 (5.0 wt. % nano-ZrO₂) increases. The main crystalline phases of samples Z1 and Z2 all are c-ZrO₂ and MgAl₂O₄. In the sample Z3 with addition of 7.5 wt. % nano-ZrO₂, a new phase, m-ZrO₂, is formed. It shows that a small amount of nano-ZrO₂ cannot form the ZrO₂-CaO solid solution due to the lack of CaO stabilizer in sample, and the peak intensity of m-ZrO₂ is also very weak. Hence, ZrO₂-MgAl₂O₄ ceramics containing c-ZrO₂ can be successfully fabricated at 1580°C for 4 h from the powders of Al₂O₃, MgO, CaO and nano-ZrO₂ by the single-stage SRS method.



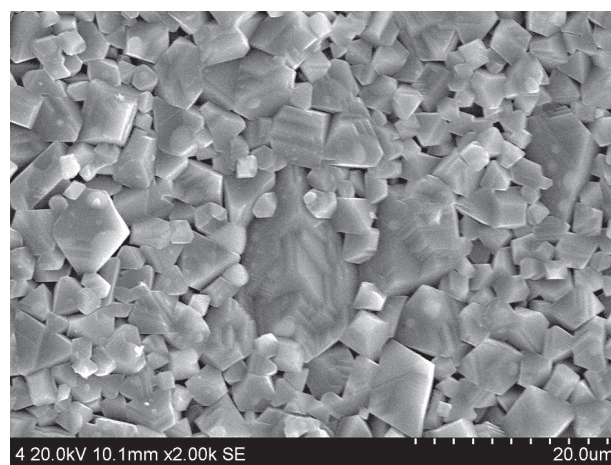
a)



b)



c)



d)

Figure 2. SEM images of as-prepared ZrO₂-MgAl₂O₄ ceramic samples doped with: a) 0 wt. %, b) 2.5 wt. %, c) 5.0 wt. % and d) 7.5 wt. % nano-ZrO₂ and sintered at 1580°C for 4 h.

Microstructures

Figure 2 shows SEM images of as-prepared ZrO_2 – MgAl_2O_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_2O_4 particles exist as granular shape. Their mean particle size is about $5\ \mu\text{m}$, and their grain sizes range from 1 to $10\ \mu\text{m}$. When 2.5 wt. % ZrO_2 was doped (Figure 2b), uniform and compact microstructure of sample Z1 is formed. The mean grain size of

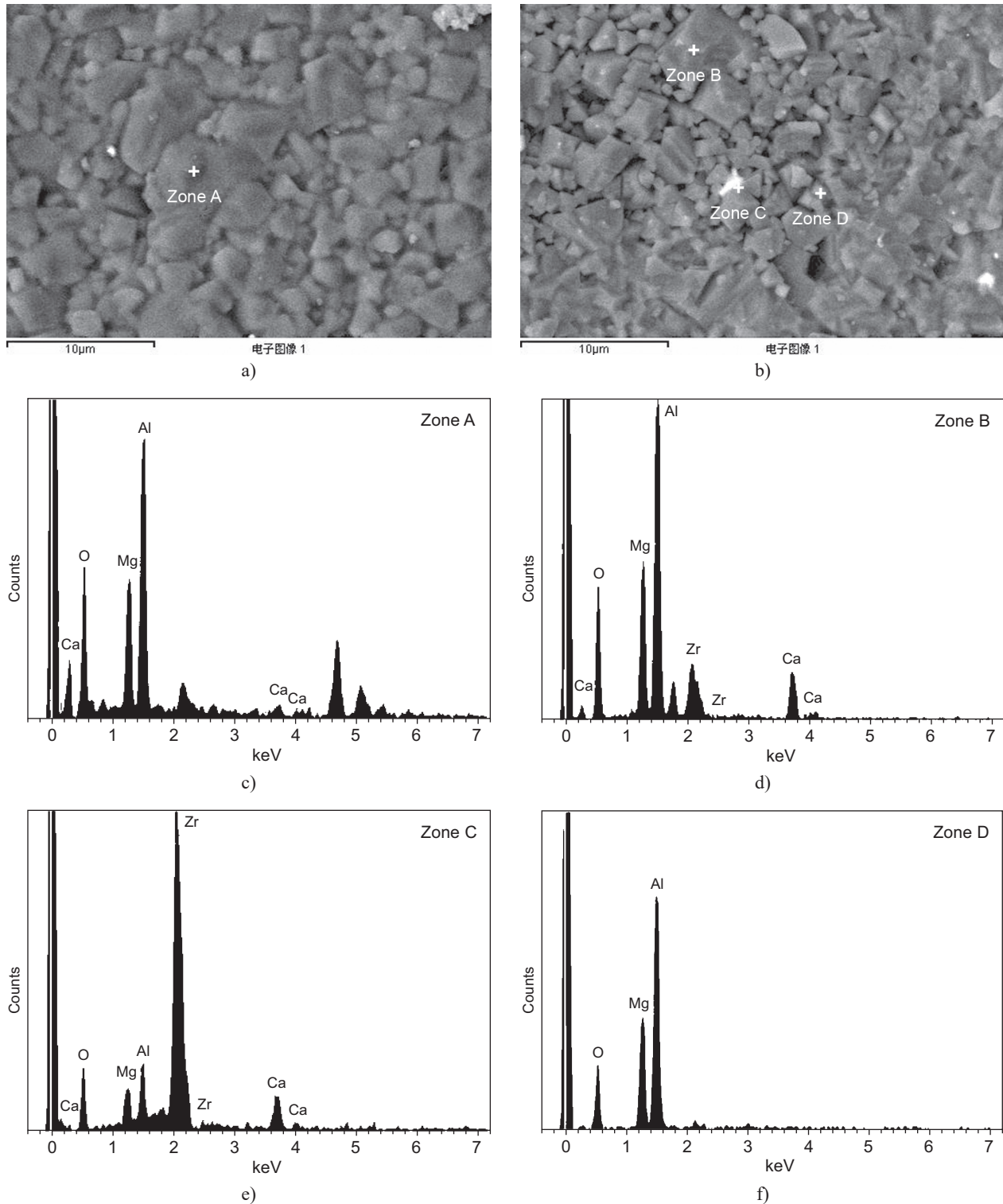


Figure 3. Back-scattering photos of as-prepared ZrO_2 – MgAl_2O_4 ceramic samples doped with: a) 0 and b) 5.0 wt. % nano- ZrO_2 and sintered at 1580°C for 4 h, and EDS patterns of zones A, B, C and D shown in Figure 3a, b.

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 microstructures 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 MgAl₂O₄-Ca_{0.15}Zr_{0.85}O_{1.85} composite body (Figure 3b). Moreover, white and small particles are c-ZrO₂ (Ca_{0.15}Zr_{0.85}O_{1.85}) (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.

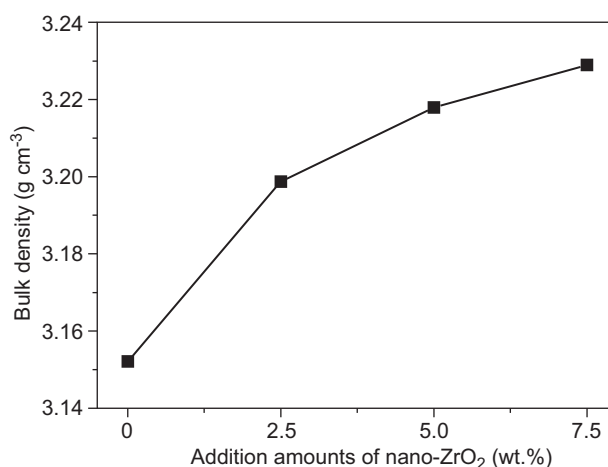


Figure 4. Effect of addition amounts of nano-ZrO₂ on the bulk density of as-prepared ZrO₂-MgAl₂O₄ ceramic samples sintered at 1580°C for 4 h.

During the sintering process of MgO-MgAl₂O₄ ceramics containing ZrO₂ additive, Zr⁴⁺ goes into MgO lattice to form a ZrO₂-MgO solid solution, which creates magnesium 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 (ΔG^θ , J·mol⁻¹) and temperature (T , K) are as follows [23, 24].

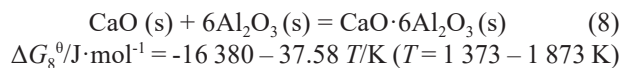
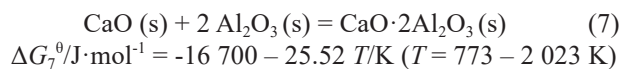
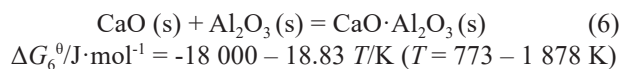
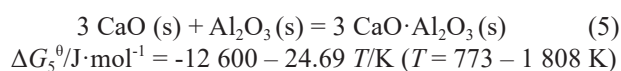
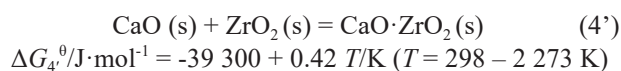
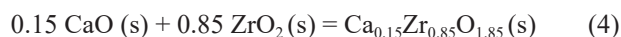
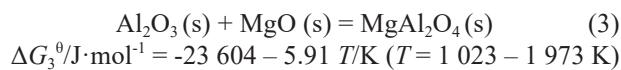


Figure 5 shows $\Delta G^\theta - T$ curve for Al₂O₃-MgO-CaO-ZrO₂ system plotted according to reactions 3–8 and their relationship expressions between ΔG^θ and T . In this study, the experimental temperature is 1 580°C (1853 K), so the ΔG^θ values at 1 853 K (dash line in Figure 5) ordered by size are $\Delta G_8^\theta < \Delta G_7^\theta < \Delta G_6^\theta < \Delta G_4^\theta < \Delta G_3^\theta$, 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 ΔG_5^θ value of $T > 1808$ K cannot be calculated due to the thermodynamic expression is used in T between 773 and 1808 K, so the curve of reaction 5 at $T > 1808$ K is plotted as dotted line.

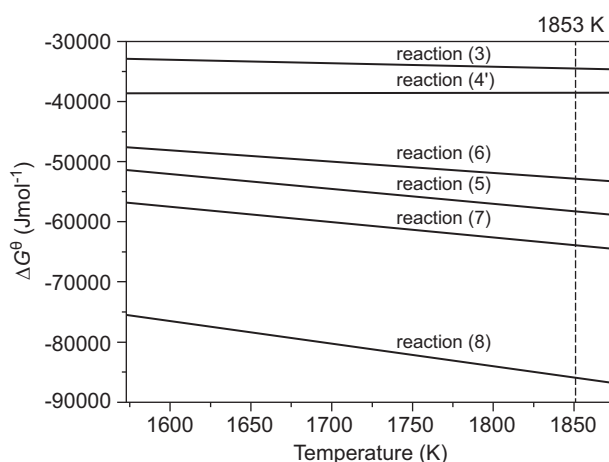


Figure 5. Change curves of $\Delta G^\theta - T$ for Al_2O_3 – MgO – CaO – ZrO_2 system.

It is clearly observed from the XRD patterns shown in Figure 1 that the main crystalline phases involve MgAl_2O_4 and c-ZrO_2 ($\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$), which are produced by reactions 3 and 4. Cubic- ZrO_2 ($\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$) is formed due to the presence of CaO stabilizer. Moreover, CaO also reacts with Al_2O_3 in raw materials to form CaAl_2O_4 secondary crystalline phase by reaction 6. In the present work, other CaO – Al_2O_3 compounds such as $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ and $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ are not detected.

In a word, the formation process of ZrO_2 – MgAl_2O_4 ceramics includes the formation of MgAl_2O_4 and the conversion process of m-ZrO_2 into c-ZrO_2 under the action of CaO stabilizer.

CONCLUSIONS

- A stoichiometric MgAl_2O_4 spinel with a bulk density of $3.15 \text{ g} \cdot \text{cm}^{-3}$ can be prepared following a single-stage SRS process at 1580°C for 4 h from a powder mixture of commercial Al_2O_3 and calcined MgO .
- The introduction of nano- ZrO_2 can remarkably promote the sintering densification of ZrO_2 – MgAl_2O_4 ceramics and improve the microstructures, and dense ceramics with bulk density of $3.23 \text{ g} \cdot \text{cm}^{-3}$ were successfully prepared when sintered at 1580°C for 4 h.
- The as-prepared ZrO_2 – MgAl_2O_4 ceramics mainly include MgAl_2O_4 and c-ZrO_2 (cubic- $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$) phases. The mean grain size of MgAl_2O_4 particles is about $2 \mu\text{m}$.
- The formation process of ZrO_2 – MgAl_2O_4 ceramics includes the production of MgAl_2O_4 , and the conversion of m-ZrO_2 to c-ZrO_2 under the stabilizing action of CaO .

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