Effect of Sintering on Phase Transformation Behavior and Morphology of Calcinated 5 Wt% Mg-PSZ

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Abstract

The zirconia structure can undergo a transformation during cooling after the sintering. The zirconia phase is stabilized by adding a doped magnesia stabilizer to the zirconia matrix. This study observed the effect of calcination temperature on the synthesis of Mg-PSZ on its phase transformation. The synthesis process was carried out with various calcinated temperatures of 600, 800 and 1000°C, with a concentration of MgO 5 wt%. Based on XRD analysis, Mg-PSZ crystal size was in the nanometer scale. The Mg-PSZ phases with 5% MgO at calcinated temperatures of 600, 800 and 1000°C were cubic, tetragonal and monoclinic respectively with each space group being Fm3m, P42/nmc and P21/c.

In addition to the phase transition, the calcination temperature also affected the crystallinity of Mg-PSZ; the higher is calcination temperature, the lower is crystallinity. Based on TEM analysis at a calcination temperature of 800°C, the Mg-PSZ microstructure showed predominantly spherical nanoparticles.

Keywords: Zirconia, Magnesia, Mg-PSZ, Phase transformation.

Introduction

Partially stabilized zirconia (PSZ) is known as an interesting material due to its fascinating physical, mechanical, electrical, chemical, thermal and bioactive properties[27] such as good flexural strength[20], high toughness[6], excellent wear resistance[1], high thermal shock resistance[24], good ionic conductivity[28], inert and biocompatibility[12]. Metal oxide stabilized zirconia has been widely used in the manufacture of electrolytes in solid oxide fuel cells (SOFC), pH sensor at high temperature, oxygen sensor, an orthopedic device, materials restorations and as an abrasive material[2]. Thus, PSZ frequently finds applications in thermal barrier coatings[3], refractories[15], oxygen-permeating membranes[28], dental and bone implants[19].

The crystal structure transformations involving volume changes exhibited thermal hysteresis which may cause cracking defects[14]. The *t→m* transformation occurring during cooling after sintering is detrimental to sintered zirconia integrity as this process is accompanied by a large increase in volume leading to disintegration by crack formation and propagation. By alloying zirconia with adequate elements, the stabilization of tetragonal or cubic phases at room temperature can be achieved[17]. The ZrO_2 phase can be stabilized by adding a stabilizer in the form of metal oxide doped into the lattice structure[18]. The metastable ZrO_2 phase is stabilized due to the presence of doping metal ions as a stabilizer, so that there is a defect in the zirconia lattice[21].

The stability of the refractory can be described by the following sequence: $Y_2O_3 > CaO > ZrO_2 > Al_2O_3 > MgO$. It is apparent that Y_2O_3 is the most stable crucible lining material, but Y_2O_3 is fairly expensive which is a drawback[14]. As a comparison to YSZ, previous studies showed that Mg-PSZ revealed promising characteristics in some aspects, namely better mechanical and thermal properties[28], good stability in low-temperature degradation (LTD) of ZrO_2 ceramics[24] and a comparable thermal-expansion coefficient[7].

Many methods have been proposed in the synthesis of Mg-PSZ including hydrothermal[22], sol-gel[10], spray pyrolysis[13], co-precipitation[16] and chemical vapor synthesis[11]. Nevertheless, most of these methods use high purity grade chemicals such as salt and alkoxide precursors and may require specific design instruments resulting in high cost and less economic values. For instance, the usage of a local raw material like zircon sand as ZrO_2 precursor is suggested and should reduce the cost in the preparation of Mg-PSZ.

The particle size of Mg-PSZ is an important parameter because the thermal conductivity is highly dependent on the particle size[11]. In this study, the template serves as a covering compound that will reduce the tendency of agglomeration[1]. Polyethylene glycol (PEG) has been reported to be successful as a cover compound in the synthesis of metal oxide stabilized zirconia. The chain of PEG ensures that the metal ions are homogeneously distributed and do not agglomerate or precipitate in solution so that nano-sized metal oxide stabilized zirconia are obtained[4].

In this study, the optimized calcination conditions for the 5wt% Mg-PSZ refractory are proposed and look at how the calcination temperature influences the transformation of the Mg-PSZ phase structure.

Material and Methods

Material and Instrument: The materials used in this study were the local zircon of West Borneo, $(NH_4)_2CO_3$, a 96%

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H_2SO_4 solution, PEG-6000 and $MgSO_4 \cdot 7H_2O$ from Merck. Inc. All materials were used without further purification. The laboratory apparatus used in this study was an IKA dual-speed mixer model RW 20 DZM with a maximum speed of 2000 rpm, a Nobertherm electric furnace with a maximum temperature of 1700°C. Meanwhile, the instruments used for the material characterization were: a Bruker D8 Advance x-ray diffractometer and a JEM-1400 120 kV TEM.

Method: The original pH of the prepared zirconium hydroxide gel precursor was pH 5. Before the synthesis of Mg-PSZ using the polyethylene glycol (PEG), template was carried out, the gel precursor pH was initially adjusted to pH 3. A 96% H_2SO_4 solution was used to dissolve the gel precursor, resulting in a zirconium salt solution at pH 1. $(NH_4)_2CO_3$ was added into the precursor salt solution until its pH attained pH 3. Magnesium salt solution was prepared separately from the gel precursors. The amount of $MgSO_4.7H_2O$ had to produce the desired weights % of MgO.

According to the design composition, the appropriate amount of the Mg-precursor solution was then added into the Zr-precursor solution under vigorous stirring, resulting in a homogenous solution. Then, 10% (w/v) PEG-6000 solution was added to the PSZ precursor. The solution mixture was stirred under heating at 100°C for 3 h. Then, the gel was filtered and dried in an oven. After that, the gel was calcinated at 600, 800 and 1000°C. Furthermore, the results of the calcination were characterized by XRD and TEM.

Results and Discussion

XRD Investigation on Mg-PSZ: XRD (Bruker D8 Advance X-ray diffractometer) is attached with Cu Kα (λ=1.5406 Å), 40 kV and 40mA. Figure 1 shows the results of the XRD identification of Mg-PSZ calcined at 600, 800 and 1000°C. The phase transformation of Mg-PSZ was analysed using X-powder software. Table 1 shows the lattice parameters of the MgPSZ structure.

Mg-PSZ calcined at 600°C showed a diffraction pattern that revealed the presence of *c*-ZrO_2 and *t*-ZrO_2 phases according to JCPDS PDF2 no. 270997 and 791770. Most of the major peaks of both the t-ZrO_2 and the c-ZrO_2 phases overlapped. The *c*-ZrO_2 phase was seen with diffraction peaks at diffraction angles 2θ of 30.40°, 50.57° and 60.34° which confirmed the planes (111), (220), (311). Meanwhile, the *t*-ZrO_2 phase as seen from its diffraction peaked at 2θ of 30.40°, 50.25°, 50.74° and 60.20°, adjusting the plane (101), (112), (200), (211). The phase of MgO was shown at 2θ, 43,07°.

Mg-PSZ calcined at 800°C showed the *t*-ZrO_2 phase according to JCPDS PDF2 No. 791770. The *t*-ZrO_2 phase was seen from its diffraction peak at a diffraction angle 2θ of 30.40°, 35.5°, 50.25°, 50.74°, 60.20°, 63.10° according to the plane (101), (110), (112), (200), (211) and (202). The increasing sintering temperature causes the transformation of the cubic to the tetragonal phase. This finding is clearly different from the report[8]. *m*-ZrO_2 and MgO are the phases formed in the zirconia-magnesia system after combustion at temperatures from 600°C to 900°C using ZrO_2 and MgO as raw materials with doped concentrations of about 1-24% by weight.

Issues regarding different yields based on the synthesis conditions such as precursor type, template, pH, medium, temperature and process reaction. In addition, the results of XRD analysis showed that the *c*-MgO phase was still present in all 800°C calcined Mg-PSZ samples.

XRD results of Mg-PSZ calcined at 1000°C consist of *t*-ZrO_2 and *m*-ZrO_2 which comply with JCPDS PDF2 No. 791770 and 830944. The presence of *m*-ZrO_2 phase in Mg-PSZ samples was indicated at 2θ of 24.1°, 28.4°, 31.48°, 33.9°, 35.5° associated with the plane (011), (−111), (111), (002), (200). The *t*-ZrO_2 phase detected with the main peak diffraction at a diffraction angle, 2θ, 30.34° and 50.2° corresponded to the plane (101) and (112). The phase transformation of Mg-PSZ from tetragonal to monoclinic can be due to the presence of the *c*-MgO phase in Mg-PSZ assumed to start to combine and enter to fill the empty ZrO_2 crystal lattice, producing a solid solution at a temperature higher than 1000°C[27].

The effect of the MgO stabilizer in stabilizing the cubic and tetragonal ZrO_2 phases at low temperatures is explained by the difference in charge between the Zr^{4+} ion and the stabilizer cation or between the oxygen anion and the oxygen vacancy. The stabilization process is caused by the presence of defects in the lattice of a crystal due to doping ions having lower valence. Each Mg^{2+} dopant cation has one oxygen vacancy. Vacancies of oxygen in the zirconia lattice can reduce the metastable phase transformation temperature, stabilize and increase the concentration of cubic and tetragonal phases in the Zr-ZrO_2 binary system region[27].

The amount of oxygen vacancies in the ZrO_2 lattice affects the stability of the formation of the tetragonal and cubic phases. The tetragonal phase is formed with a lower number of oxygen vacancies while the cubic phase is formed with a higher number of oxygen vacancies[5]. At calcination of 600°C, the oxygen vacancy is high due to the inclusion of the MgO phase which has one oxygen vacancy into the ZrO_2 lattice as a result of low-temperature calcination. This increase in oxygen vacancy lowers the transformation temperature so that it stabilizes *c*-ZrO_2 at low temperatures[26]. The increased calcination causes a transformation from *c*-ZrO_2 to *t*-ZrO_2 explaining that increasing the calcination to 800°C causes a decrease in oxygen vacancy in the ZrO_2 lattice. When the vacancy oxygen concentration is low, the ZrO_2 structure is distorted towards the tetragonal phase[9].

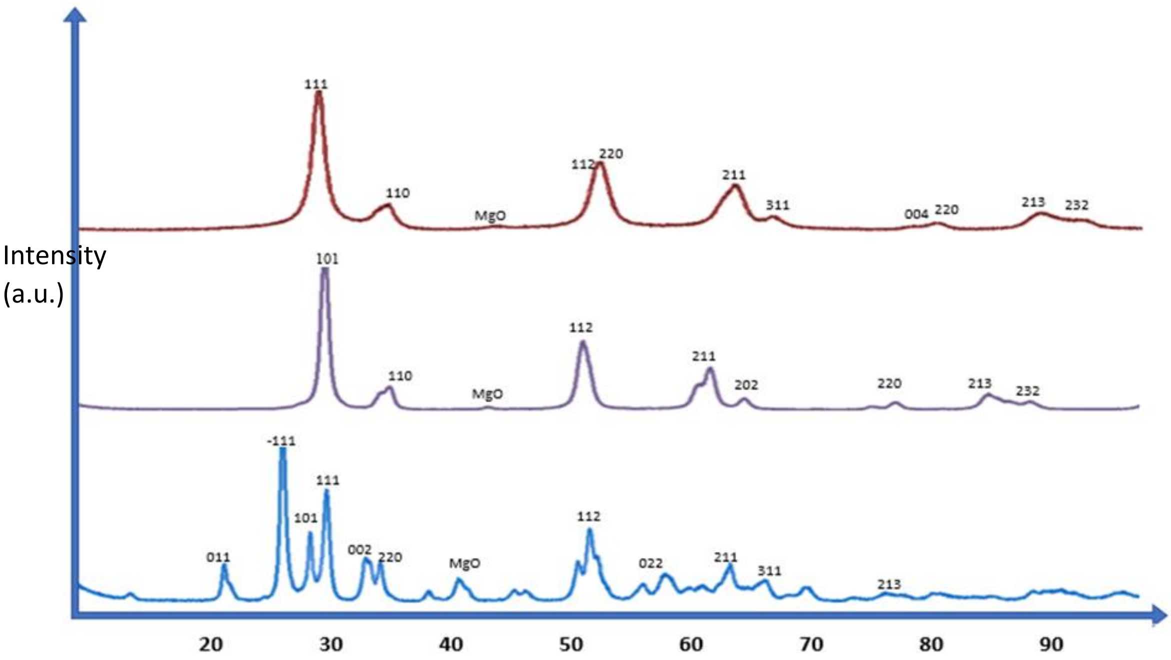

Figure 1: XRD pattern of Mg-PSZ calcinated at 600, 800 and 1000°C

Table 1
Lattice parameter of Mg doped zirconia

Parameters	**Mg-PSZ 600°C**		**Mg-PSZ 800°C**	**Mg-PSZ 1000°C**	
Crystal System	Cubic	Tetragonal	Tetragonal	Tetragonal	Monoclinic
Space Group	*Fm3m*	*P42/nmc*	*P42/nmc*	*P42/nmc*	*P21/c*
a (Å)	5.0900	3.5936	3.5936	3.5936	5.1440
b (Å)	5.0900	3.5936	3.5936	3.5936	5.1330
c (Å)	5.0900	5.1814	5.1814	5.1814	5.347
Density (g/cm^3)	6.206	6.166	6.166	6.166	5.867

Table 2
Crystallite size and crystallinity Mg-PSZ from XRD analysis

Sample	**Crystallite size (nm)**	**Crystallinity (%)**
Mg-PSZ 600°C	9	90.62
Mg-PSZ 800°C	13	91.23
Mg-PSZ 1000°C	21	73.83

At higher calcination of 1000°C, a phase transformation occurred to *m*-ZrO_2, which was associated with crack propagation of the *t*-ZrO_2 structure when the temperature was increased. Crack propagation causes phase transformation of *t*-ZrO_2 to *m*-ZrO_2[26]. This crack propagation is evidenced by a decrease in the crystallinity of Mg-PSZ. Table 2 shows the crystallinity of Mg-PSZ when the calcination was varied at 600, 800 and 1000°C.

Mg-PSZ Microstructure: The microstructure of Mg-PSZ was only seen at 800°C. Based on XRD, it is known that Mg-PSZ was nano-size (Table 2). The microstructure of the Mg-PSZ showed that it consisted of spherical particles. The presence of a PEG template affects the morphology of the Mg-PSZ particles. PEG long chains play a role in ensuring that metal ions are homogeneously distributed and prevent agglomerate or precipitate in solution so that nano-sized magnesia stabilized zirconia is obtained[4].

The presence of PEG in restraining particle interactions is through the mechanism of hydrogen bonding interaction between the hydroxyl group (OH) of the precursor $Zr(OH)_2 \cdot xH_2O$ with the ether group (-O-) of PEG[23]. The PEG template will envelop and cover the surface of the particles thereby reducing the occurrence of particle agglomeration due to steric hindrance from the PEG molecules[4]. This phenomenon can reduce the aggregation of synthesized Mg-PSZ samples but will slow the growth of PSZ particles during heating at high temperatures.

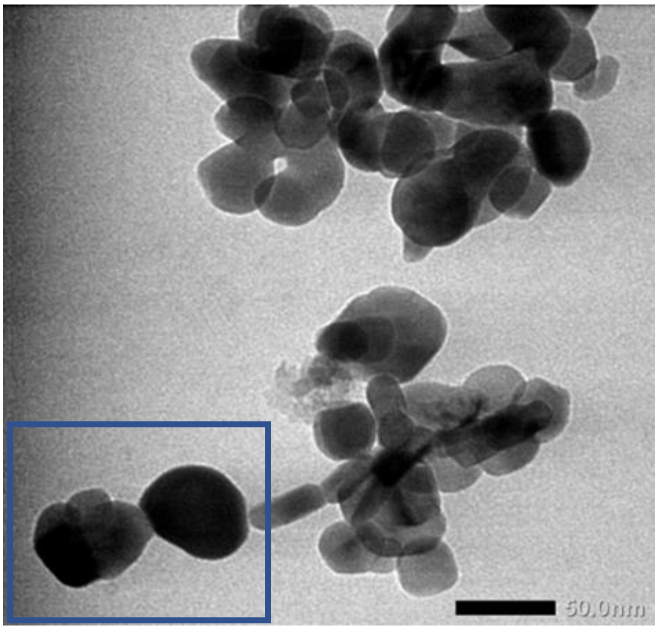

Figure 2: TEM image of 5 wt% Mg-PSZ at 800°C

Conclusion

PSZ material with MgO 5%wt dopant had a crystal size of 9-21 nm. Variations in calcination affected the formation and phase transformation of ZrO_2. The cubic phase (c-ZrO_2) was formed at a calcination temperature of 600°C, while the tetragonal phase (t-ZrO_2) was formed at 800°C and the monoclinic phase (m-ZrO_2) at a temperature of 1000°C. This phase transformation caused the crystallinity of Mg-PSZ to change.

At 800°C calcination, Mg-PSZ had the highest crystallinity, while the lowest crystallinity was at 1000°C calcination temperature. The microstructure of the Mg-PSZ sample showed a spherical particle shape caused by the presence of a PEG template.

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