Crystallization and grain growth behavior of La$_2$O$_3$-doped yttria-stabilized zirconia

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The effect of La$_2$O$_3$ addition on the microstructure and grain growth behavior of yttria-stabilized zirconia (8YSZ) was investigated. To this end, 8YSZ was doped with 1–15 wt% La$_2$O$_3$ by means of colloidal processing, and then sintered at 1550 ºC for 1 h. XRD results identified a dissolution limit of 5 wt% La$_2$O$_3$ in 8YSZ, the insoluble La$_2$O$_3$ at higher concentrations reacting with ZrO$_2$ during sintering to form a secondary La$_2$Zr$_2$O$_7$ phase. Both undoped and La$_2$O$_3$-doped 8YSZ specimens were annealed at 1400, 1500, and 1600 ºC for 10, 50, and 100 h to induce grain growth. Grain growth measurement results showed that an increase in annealing temperature and holding time caused to grain growth in all specimens. Excessive grain growth was observed in the case of the undoped, and 1.5 wt% La$_2$O$_3$-doped 8YSZ specimens; however, the grain growth in 10 and 15 wt% La$_2$O$_3$-doped 8YSZ was inhibited by the formation of a pyrochloiric La$_2$Zr$_2$O$_7$ secondary phase around the grains and grain boundaries of 8YSZ. Grain growth exponent ($n$) and activation energy ($Q$) values for grain growth of undoped 8YSZ were obtained as 3, and 358 kJ/mol, respectively, while 15 wt% La$_2$O$_3$ containing specimens had a grain growth exponent of 3, and activation energy of 413 kJ/mol. These results indicate that grain growth rate can be controlled by the addition of 10 or 15 wt% La$_2$O$_3$. Copyright © 2014 VBRI press.

Keywords: Yttria-stabilized zirconia (8YSZ); pyrochloiric La$_2$Zr$_2$O$_7$; grain growth; solid oxide fuel cell (SOFC).

Introduction

Zirconia (ZrO$_2$)-based oxide ceramics are one of the best known and most widely used oxygen ion conductors employed in commercial fuel cells, oxygen sensors, and oxygen pumps [1]. Pure ZrO$_2$ is an insulating material that undergoes a number of phase transformations upon heating, it exists as monoclinic crystal from room temperature to 1170 ºC, above which the monoclinic zirconia (m-ZrO$_2$) transforms into a tetragonal crystal structure; this transformation is accompanied by a volume reduction of 5%. At around 2370 ºC, the tetragonal crystal structure transforms into cubic crystal structure. This cubic zirconia (8YSZ) is stable up to 2680 ºC, which is the melting temperature of zirconia. The volume change caused during the phase transformations induces a large amount of stress, which tends to crack ZrO$_2$ upon cooling from high temperatures [2]. Consequently, ZrO$_2$ is typically blended with lower-valence oxides such as CaO [3], Y$_2$O$_3$ [4], Gd$_2$O$_3$ [5], Sc$_2$O$_3$ [6] and La$_2$O$_3$ [7] to form a solid solution.

Pyrochloiric R$_2$Zr$_2$O$_7$ (R = rare-earth-metal) compounds have been used as hosts for fluorescence centers and oxidation catalysts, and thus, a number of investigations have been conducted to evaluate the electrical, optical, and
catalytic properties of such materials [8–10]. Particular attention has been given to the pyrochlore La$_2$Zr$_2$O$_7$, which has been found to form at the cathode (La$_{1-x}$Sr$_x$MnO$_3$) / electrolyte (yttria-stabilized zirconia: YSZ) interfaces of solid oxide fuel cells (SOFCs) during high-temperature processing [11, 12]. This phenomenon has been investigated as a means of synthesizing La$_2$Zr$_2$O$_7$ by a number of different methods, including solid-state reaction [13, 14], nitric acid dissolution, and the sol-gel technique [13, 15, 16]. However, the formation of pyrochlore La$_2$Zr$_2$O$_7$ has thus far only been achieved by the sol–gel process [15]. The ZrO$_2$–La$_2$O$_3$ system therefore not only provides stabilization of high-temperature structures, but also includes the pyrochloiric-structured La$_2$Zr$_2$O$_7$ [17, 18]. This means it has potential for application as both a catalyst [10] and a thermal barrier [19], and it can also be synthesized by either a solid-state reaction between oxides at 1500–1600 °C, or by the sol–gel process [15].

In the case of solid-state reaction, grain growth occurs in ceramics during the sintering and high-temperature annealing processes. Since the mechanical properties of coarse-grained ceramics are lower than those of fine-grained ones [20–23], a number of methods have been developed to prevent grain coarsening and to stabilize the microstructure. These prevent grain growth by making composite ceramics containing additives that facilitate sintering, in addition to using a cold and hot isostatic pressing processes [24]. It has been previously reported that the excessive grain growth in yttria-stabilized cubic zirconia (8YSZ) is associated with a low rate of Y$_2$O$_3$ precipitation at the grain boundaries. This in turn leads to a low cohesive strength between grain boundaries and a high grain boundary energy in the 8YSZ [25]. Consequently, in order to prevent grain growth, grain boundary mobility must be prevented and the grain boundary energy of the 8YSZ must be reduced. 8YSZ is well known for its high ionic conductivity and chemical stability across a range of different temperatures and oxygen partial pressures [26]; thus, it is widely used as an oxygen sensor [27, 28] and as a solid electrolyte in SOFCs [29]. In such applications, there is need not just for high conductivity, but also for greater mechanical, chemical, and electrical stability [30]. Due to the need for a high operating temperature (1000 °C) in SOFCs, the operating efficiency is greatly reduced [31]. Furthermore, the mechanical strength of 8YSZ is also reduced as a result of holding at high temperatures for long periods of time, which greatly restricts the use of the material as a solid electrolyte. These heat stresses, combined with the mechanical stresses caused by working and excessive grain growth, mean that 8YSZ used under such conditions tends to break quite easily [32]. Improving the mechanical properties of 8YSZ for use as a solid electrolyte is therefore an important problem that still needs to be solved.

Consequently, the objective of this study is to prevent grain growth of 8YSZ through the addition of La$_2$O$_3$, thus improving its mechanical properties and suitability for use as a solid electrolyte. The choice of La$_2$O$_3$ as a dopant was based on the mismatch between the ionic radii of ZrO$_2$ and La$_2$O$_3$, and the fact that their valences are nearly equal. The effect of varying the amount of La$_2$O$_3$ addition on the phase equilibrium, microstructure, sintering, and grain growth of 8YSZ was subsequently investigated.

**Experimental**

**Materials**

For the matrix, 8 mol% of high-purity (>99.999%) 0.3 μm yttria-stabilized cubic zirconia (8YSZ) (Tosoh, Japan) powder was used, while up to 15 wt% of high-purity (>99.9%) 0.25 μm La$_2$O$_3$ (Mbc Industrial Co., China) powder was used as an additive. The chemical compositions of each powder are listed in **Table 1**.

**Table 1.** The chemical composition of the powders used in the experimental works.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Zr$_2$O$_7$</th>
<th>Y$_2$O$_3$</th>
<th>La$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>FeO$_3$</th>
<th>Nb$_2$O$_5$</th>
<th>CaO</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8YSZ</td>
<td>85.9</td>
<td>13.6</td>
<td>-</td>
<td>0.1</td>
<td>0.003</td>
<td>0.01</td>
<td>0.02</td>
<td>0.25</td>
<td>0.1</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>-</td>
<td>-</td>
<td>99.99</td>
<td>0.003</td>
<td>-</td>
<td>0.005</td>
<td>-</td>
<td>0.002</td>
<td></td>
</tr>
</tbody>
</table>

**Colloidal processing and production of samples**

The specimens for microstructural investigation were produced by means of colloidal processing. The doping process was carried out in a plastic container through the mechanical mixing of 8YSZ and up to 15 wt% La$_2$O$_3$ with zirconia balls and ethanol. The mechanical mixing was performed in a “speks” type mixer at 200 rpm for 12 h. The prepared slurries were left to dry for 24 h by simply leaving the mixer lid open. Once dry, the agglomerated powders with medium hardness were ball milled for 10 minutes to obtain a good dispersion and to break up the agglomerates. The resultant powders were passed through a 60 μm sieve and then pressed under 200 MPa of pressure in a single-axis die with a radius of 10 mm and a height of 4 mm. The inner surface of the steel die was cleaned after each drying process and stearic acid was applied to the side walls of the die as a release agent.

**Sintering and density measurement of samples**

Sintering was carried out in a box-type furnace under normal atmospheric conditions. The pressed pellets were first subjected to a pre-sintering process at 1000 °C, and then sintered at a temperature 1550 °C for 1 h with a heating and cooling rate of 5 °C /min. The density of the sintered specimens was calculated by assuming a perfect state reaction between oxide compositions of each powder are listed in **Table 1**.
specimens sintered at an optimum temperature was evaluated by annealing at 1400, 1500, and 1600 °C for 10, 50, and 100 h. The surfaces of the specimens were ground and polished using normal metallographic methods after sintering, and were then thermally etched by holding in a furnace at 50 °C below the sintering temperature for 1 h. The microstructural investigation of the sintered specimens was performed using a scanning electron microscope (SEM, Jeol Lv 6060). The grain sizes of the specimens were measured by the mean linear intercept method and the average for each specimen was determined using the following equation:

\[ D = \frac{L_i}{N_i \cdot M} \]  

where \( L_i \) is the length of the line, \( N_i \) is the number of grain-boundary intercepts, and \( M \) is the magnification in the photomicrograph of the material.

**Results and discussion**

Fig. 1 shows the XRD patterns obtained from 8YSZ specimens doped with various amounts of La\(_2\)O\(_3\). From this, it can be seen that those specimens containing 1 and 5 wt% La\(_2\)O\(_3\) are composed of only a single cubic-structured crystal phase. Furthermore, no La\(_2\)O\(_3\) peaks were observed in these specimens, indicating that La\(_2\)O\(_3\) was completely dissolved in the 8YSZ matrix and did not remain as a secondary phase around the grains or grain boundaries of 8YSZ. However, when more than 5 wt% La\(_2\)O\(_3\) is added, peaks emerge corresponding to pyrochlore La\(_2\)Zr\(_2\)O\(_7\) that indicate the overdoped La\(_2\)O\(_3\) is not solubilized in the 8YSZ matrix, but rather forms a secondary La\(_2\)Zr\(_2\)O\(_7\) phase at high temperatures.

SEM and EDS analyses revealed that this new phase is preferentially precipitated around the grains and grain boundaries of 8YSZ. Moreover, the XRD results show that the La\(_2\)Zr\(_2\)O\(_7\) is composed of hexagonal and cubic crystal structures. Some of the peaks of the 8YSZ specimens doped with 10 and 15 wt% La\(_2\)O\(_3\) can be indexed to a cubic-pyrochlore-structured La\(_2\)Zr\(_2\)O\(_7\) and a hexagonal-crystal-structured La\(_2\)Zr\(_2\)O\(_7\), which is in agreement with JCPDS 30-1468 and JCPDS 17-0450 (International Center for Diffraction Data Files). The formation of pyrochlore La\(_2\)Zr\(_2\)O\(_7\) is likely due to the difference in the ionic radii and crystal structures of La\(_{3+}\) and Zr\(_{4+}\) ions; it is well-known that the ionic radius of La\(_{3+}\) with a hexagonal structure is 1.016 Å, while that of Zr\(_{4+}\) with a cubic crystal structure is 0.84 Å. The pyrochlore structure is therefore defined as two distinct and intertwined structures that are distinguished as a cation-centered octahedral ZrO\(_6\) and an anion-centered tetrahedral La\(_4\)O. The La\(_2\)Zr\(_2\)O\(_7\) is formed by the unification of one tetrahedral and two octahedral structures, with La\(_{3+}\) cations situated in a hexagonal window of the octahedral lattice [32, 33].
of growth increasing annealing temperature and holding time. The undoped 8YSZ specimen and those doped with 1 and 5 wt% La$_2$O$_3$ exhibit an equiaxed, faceted, uniform, and coarse-grained structure (Fig. 2A-C), whereas those samples with 10 and 15 wt% La$_2$O$_3$ have faceted 8YSZ grains, together with smaller spherical grains of La$_2$Zr$_2$O$_7$ (Fig. 2D-E). Furthermore, it can be observed in Fig. 2 that the porosity level increases with increasing La$_2$O$_3$ content.

The grain growth kinetics was determined using the following equations:

$$D^n - D_0^n = K(t - t_0)$$  \hspace{1cm} (2)

$$K = K_0 \exp\left(-\frac{Q}{RT}\right)$$  \hspace{1cm} (3)

where $D$ is the grain size after a period of time $t$, $D_0$ is the initial grain size, $n$ is the grain growth exponent, $K$ is a kinetic constant dependent on grain boundary and temperature, $K_0$ is a constant not dependent on temperature and $Q$, $R$ and $T$ are activation energy, gas constant and the absolute temperature, respectively. The grain growth exponent ($n$) is calculated from the slope of the line obtained from a plot of $\ln(D^n - D_0^n)/t$ vs $1/T$, as shown in Fig. 4.

The activation energies for 1, 5 wt% La$_2$O$_3$-doped 8YSZ specimens were subsequently calculated as 3 (Figure 4A-E), indicating an impurity drag controlled growth mechanism.

The grain growth exponent ($n$) values of undoped and La$_2$O$_3$-doped 8YSZ specimens are given in Fig. 4, and these vary depending on the specimen microstructure [34]. The value of $n$ is generally between 2 and 4, and when equal to 2, it exhibits a parabolic relationship in single-phase systems at high temperature. Grain growth is controlled by solid solution drag when the value of $n$ is 3, the necessary conditions for which are that one of the components of solid solution should precipitate at the grain boundaries. When the value of $n$ is 4, it indicates that the grain growth rate is controlled by pore drag; however, considered highly unlikely to be the case in this instance given the narrow grain size distribution and small porosity fraction (2–4 %) [35]. The values of $n$ for the undoped and La$_2$O$_3$-doped 8YSZ specimens were subsequently calculated as 3 (Figure 4A-E), indicating an impurity drag controlled growth mechanism.

The activation energy, $Q$, for the grain growth was calculated from the slope of the line obtained from a plot of $\ln(D^n - D_0^n)/t$ vs $1/T$, as shown in Fig. 5. These results reveal that the activation energies of 10 and 15 wt% La$_2$O$_3$-doped 8YSZ specimens are substantially higher than those of undoped 8YSZ, which is believed to be due to La$_2$Zr$_2$O$_7$ secondary phase. A higher activation energy means a lower rate of grain growth. The activation energy for undoped 8YSZ was calculated as 358 kJ/mol, whereas the activation energies for 1, 5, 10, and 15 wt% La$_2$O$_3$-doped 8YSZ specimens were calculated as approximately 334, 355, 383, and 413 kJ/mol, respectively. It can therefore be seen that the activation energies of the 1 and 5 wt% La$_2$O$_3$-doped 8YSZ specimens are in fact lower than that of undoped 8YSZ, which means that grain growth should be faster in 1 and 5 wt% La$_2$O$_3$-doped 8YSZ specimens.

This reduced activation energy in the 1 and 5 wt% La$_2$O$_3$-doped 8YSZ specimens is likely to be attributable to the high diffusion coefficient and rate of dissolution of La$_2$O$_3$ in the 8YSZ matrix.
Conclusion

XRD analysis showed that the 8YSZ specimens doped with 1 and 5 wt% La2O3 have a cubic crystal structure, and that this structure did not change with the addition of La2O3. Furthermore, these specimens did not exhibit La2O3 peaks, indicating that the La2O3 was completely dissolved in the 8YSZ matrix. However, with an increase in doping to more than 5 wt%, peaks corresponding to pyrochloidal La2Zr2O7 emerged that indicate the excess La2O3 forms a secondary phase of La2Zr2O7 at high temperatures.

Increasing the annealing temperature and holding time caused increased grain growth in both undoped and La2O3-doped 8YSZ specimens. Excessive grain coarsening was observed in the undoped, 1 and 5 wt% La2O3-doped 8YSZ specimens; however, grain growth in the 10 and 15 wt% La2O3-doped 8YSZ specimens was inhibited by the presence of the La2Zr2O7 secondary phase around the grains and grain boundaries of 8YSZ. The grain growth exponent values (n) of the undoped and La2O3-doped 8YSZ specimens obtained were found to be equal to three, indicating that grain growth was controlled by impurity drag. The activation energies for the 1, 5, 10, and 15 wt% La2O3-doped 8YSZ specimens were determined to be 334, 355, 383, and 413 kJ/mol, respectively. The activation energy was particularly increased in the 10 and 15 wt% La2O3-doped 8YSZ, confirming a reduction in grain growth when compared to undoped 8YSZ.

Acknowledgements

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Reference

22. reference