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Abstract. Solid Oxide Fuel Cells (SOFCs) are emerging as an advanced and efficient energy conversion technology that could be a solution to some of the environmental issues. SOFCs are able to produce clean electricity and heat from hydrogen energy. Due to their high ionic conductivity in the intermediate temperature range of 600 ℃ to 800 ℃, scandia stabilized zirconia is a very promising electrolyte material for SOFCs. However, the long term damage caused by cyclic heating and cooling during the stages of start-up and shut down of SOFC will greatly affect the performance of the fuel cell. The structural damages will result in poor mechanical properties which directly influence the durability of the ceramic electrolyte. Therefore, it is essential to investigate the thermal degradation behavior of various zirconia ceramic systems. In this work, the thermal degradation behavior of the zirconia ceramics are investigated by adopting thermal cycling test at two different heating rates (10°C/min and 20°C/min) to examine the durability of the zirconia electrolyte, in particular the structure degradation caused in thermal cycling. Ordered array of convex meniscus were observed on the surface of the undoped zirconia ceramics and the grain growth was suppressed during thermal cycling. The effect of thermal cycling on the mechanical stability of zirconia based ceramics were affected by the addition of 1 wt% MnO_2 which showed a reduction in the hardness and fracture toughness.

1. Introduction

The industrial interest in solid oxide fuel cells (SOFCs) has grown dramatically with the ongoing demand to reduce dependency on fossil fuels as well as developing clean and efficient energy for distributed power system. A Solid Oxide Fuel Cell (SOFC) works on the principle of direct chemical to electrical energy conversion from gaseous fuel, which is similar to a galvanic cell [1]. In the cell, anode and cathode are separated by an electrolyte that allows the transfer of oxygen ions (O^{2-}) from the cathode to the anode, where they combine with hydrogen or carbon monoxide. Many fuel cells require a clean stream of hydrogen as the fuel, but SOFCs can also use hydrocarbons directly for power generation.

Two most important oxygen ion conductors used as electrolytes for SOFCs are doped zirconia and ceria [2-5]. Doped ceria shows higher ionic conductivity compared to zirconia based electrolytes due to its six-fold open structure that allows the oxygen vacancies to migrate more freely, but electronic conduction can occur at lower oxygen partial pressures [2, 4]. Fully stabilized zirconia such as yttria (YSZ) and scandia stabilized zirconia (ScSZ) have been reported as suitable electrolytes for SOFC, with ScSZ found to higher conductivity compared to YSZ, especially for intermediate-temperature applications [6].

The ScSZ powders are usually sintered at high temperature (1400-1700°C) and require long holding time (6-15 hours) to stabilize the cubic phase and to obtain highly dense structure [6-10]. However, excessive grain growth that could happen during the high temperature sintering process adversely affects the mechanical properties. Bending strength was reported for both partially and fully stabilized zirconia, and it was found that fully stabilized zirconia has lower bending strength compared to the partially stabilized zirconia [6]. However, the other mechanical properties such as Vickers hardness or fracture toughness of the electrolyte were not assessed in most of the previous studies mentioned earlier.

Long term damage caused by cyclic heating and cooling during the stages of start-up and shut down of SOFC will greatly affect the performance of the fuel cell [11]. The structural damages will result in poor mechanical properties which directly influence the durability of the ceramic electrolyte. As yet, there is no fully satisfactory answers to thermal shock resistance of solid oxide electrolytes used in SOFCs. Therefore, it is essential to investigate this problem through the evaluation of thermal degradation behaviour of various ScSZ ceramic systems.

The aim of the present study is to investigate the effect of thermal cycling on the mechanical properties of zirconia ceramics. The ageing of zirconia ceramic would be investigated by adopting thermal cycling test at two different heating rates (10°C/min and 20°C/min) to investigate the durability of the zirconia, in particular the structural degradation caused in thermal cycling.

2. Experimental

This work focus on the analysis of mechanical properties, sintering and degradation behaviour of ceria-doped scandia stabilised zirconia ceramics. Thermal cycling test, which deals with a variation in temperature, normally between the room temperature to the elevated operating temperature was performed to simulate the abrupt changes in the zirconia ceramic while it is in operation.

The as-received commercially available 1 mol% ceria doped 10 mol% scandia stabilized zirconia (10Sc1CeSZ) ceramic powder was obtained from Daiichi Kigenso Kagaku Kogyo Co. (DKKK). The 10Sc1CeSZ powder was co-doped with 1 wt% of manganese oxide (R&M Chemicals, UK) using solid state synthesis. The powders were mixed with ethanol in a conventional ultrasonic bath and then attritor milled using 2 mm diameter zirconia balls as the grinding medium at 450 rpm for 1 hour. The slurry was dried in oven at 60 °C for overnight. The dried powders were pressed by uniaxial pressing followed by cold isostatic pressing at 200 MPa. The pressed pellets were sintered at 1600 °C for 2 hours with a heating rate of 10 °C/min. For thermal cycling, the sintered zirconia samples were subjected to 30 cycles of thermal cycling at 800°C for 30 minutes with a heating rate of 10°C/min and 20°C/min.

Scanning Electron Microscope (SEM) was used to identify the morphology of the microstructure. The densities of the specimens were evaluated by using Archimedes' principle. Vickers Hardness was calculated from the diagonal length of the indentation using Mitutoyo Vickers hardness tester (AVK-

CO). The fracture toughness was obtained by using Palmqvist crack system as the semi-elliptical cracks and the formula is [12]:

$$K_{IC} = 0.079 \left(\frac{P}{a^{3/2}} \right) log \left(4.5 \frac{a}{c} \right)$$

where P is the indentation load, a is the average diagonal length of Vickers indentation and c is the average Palmqvist crack length.

3. Results and Discussion

Figure 1 and figure 2 show the SEM images of undoped and 1 wt% MnO_2-doped 10Sc1CeSZ sintered samples, before and after 30 cycles of thermal cycling at 10 °C/min and 20 °C/min, respectively. The calculated grain size of the zirconia ceramic samples is shown in figure 3.

The grain size of the undoped 10Sc1CeSZ sintered samples were found to be smaller than 1 wt% MnO_2-doped 10Sc1CeSZ samples, with an average grain size of 7.88 ± 0.45 μm and 9.28 ± 0.98 μm, respectively, before thermal cycling. The grain size of undoped 10Sc1CeSZ sample was found to be reduced by around 12.3 % after thermal cycling, whereas grain growth of about 6.3% were observed for 1 wt% MnO_2-doped 10Sc1CeSZ samples with large pores observed at the grain boundary after thermal cycling at two different heating rates. It is believed that large amount of the manganese dopants melted during the sintering process at high temperature [13]. The melting of MnO_2 led to the significant amount of residual pores at the grain boundaries as observed in the SEM micrograph.
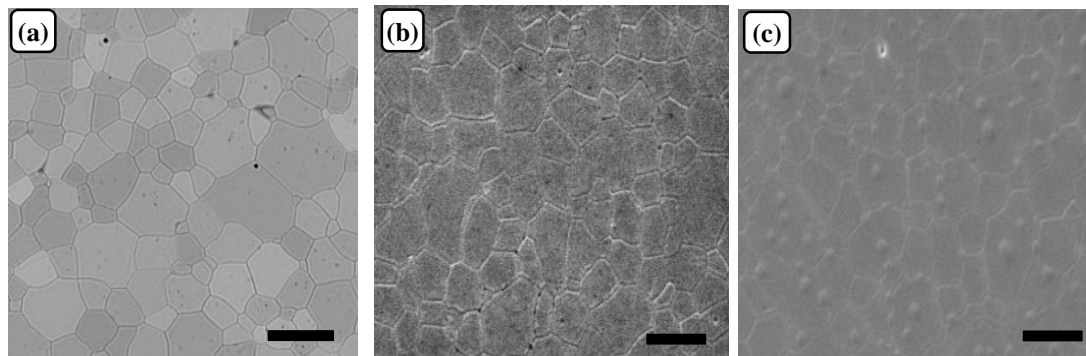

Figure1. SEM images of 10Sc1CeSZ zirconia sintered samples (a) before thermal cycling and after thermal cycling at (b) 10°C/min, (c) 20°C/min. The value of the scale bar is 10 μm.
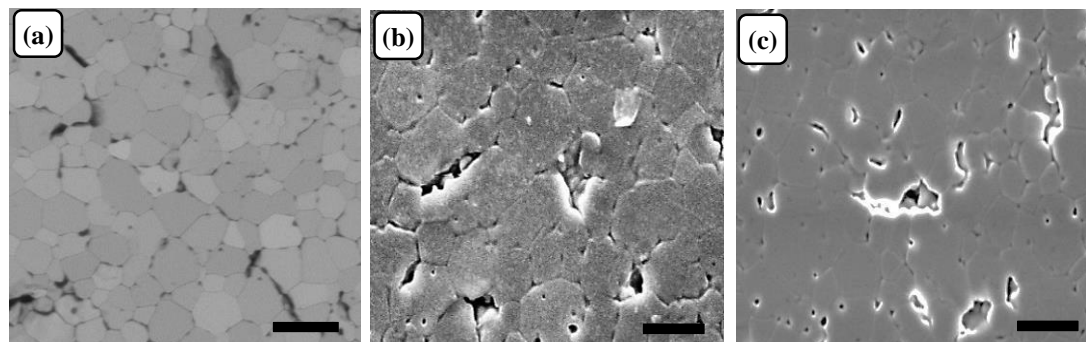

Figure 2. SEM images of 1 wt% MnO_2-doped 10Sc1CeSZ zirconia sintered samples (a) before thermal cycling and after thermal cycling at (b) 10 °C/min, (c) 20 °C/min. The value of the scale bar is 10 μm.
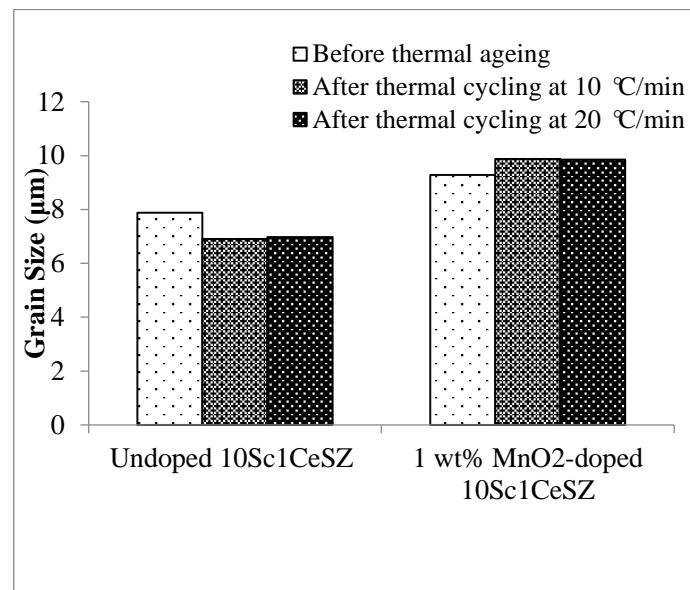
Figure 3. Grain size of undoped and 1wt% MnO_2-doped 10Sc1CeSZ zirconia ceramics sintered samples before and after thermal cycling at 10 °C/min and 20 °C/min.

There was ordered array of convex meniscus observed on the surfaces of the undoped 10Sc1CeSZ ceramic samples after thermal cycling at 20 °C/min as shown in figure 1(c). Similar spherical liquid phase beads were reported in YSZ/alumina composite samples [14]. It is postulated that siliceous phase in the zirconia ceramics were expelled to the surface of the zirconia ceramics by the rapid thermal cycling process.
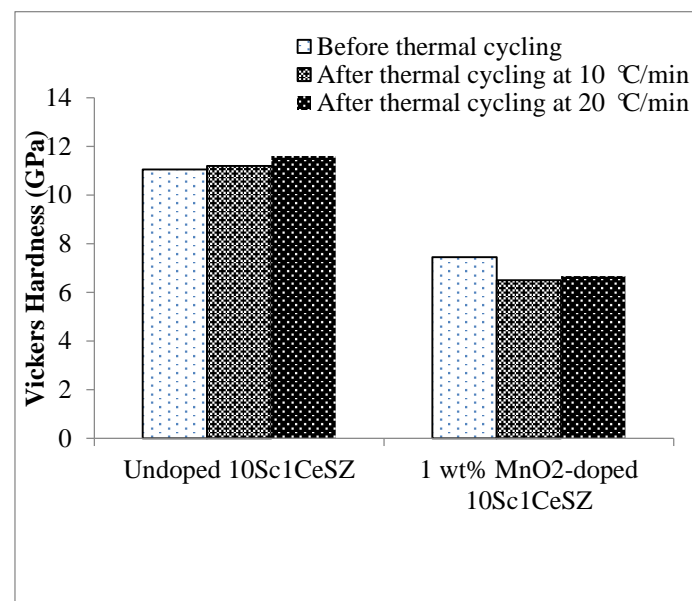

Figure 4. Vickers hardness of undoped and MnO_2-doped 10Sc1CeSZ zirconia ceramic sintered samples before and after thermal cycling at 10°C/min and 20°C/min.

Figure 4 shows that the fully dense undoped 10Sc1CeSZ had a Vickers hardness of 11.05 ± 0.34 GPa, while MnO$_2$-doped 10Sc1CeSZ with a relatively lower density (92% of the theoretical density) had a lower hardness value of 7.44 ± 0.35 GPa. The hardness result is found to be correlated well to the density. After thermal cycling, the Vickers hardness of undoped ScCeSZ increased slightly ~5.0%, whereas MnO$_2$-doped 10Sc1CeSZ samples showed a reduction of 12.8% in hardness. This is mainly due to the appearance of residual pores in the MnO$_2$-doped 10Sc1CeSZ ceramic samples after thermal cycling. The large fraction of residual porosity has adversely affected the hardness. However, it is apparent that there were no significant changes in the hardness values for both samples thermal cycled at two different heating rates.
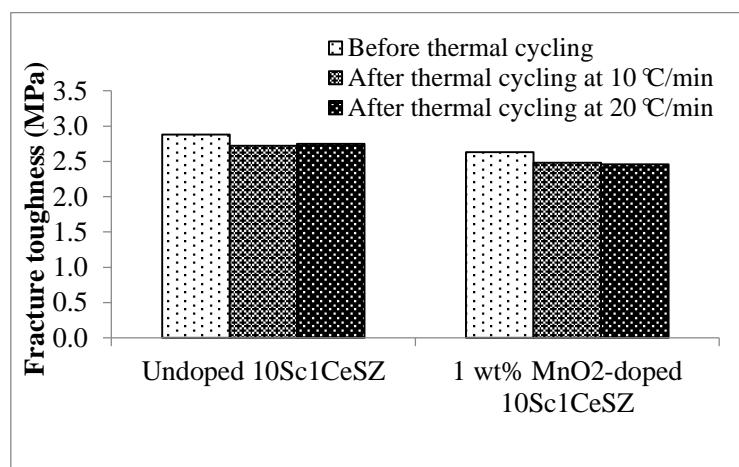

Figure 5. Fracture toughness of 10Sc1CeSZ zirconia ceramic sintered samples before and after thermal cycling at 10°C/min and 20°C/min.

Figure 5 shows that undoped 10Sc1CeSZ sintered ceramics had a slightly higher fracture toughness (2.88 ± 0.12 MPa) than 1 wt% MnO$_2$-doped 10Sc1CeSZ (2.63 ± 0.19 MPa) before thermal cycling process. However, both zirconia ceramics samples experienced a slight reduction of 5.6- 6.5% in fracture toughness after thermal cycling. From the SEM micrographs of these two samples, it can be observed that the grain boundaries of undoped 10Sc1CeSZ were better defined than the large-grained MnO$_2$-doped 10Sc1CeSZ samples after thermal cycling. Manganese is able to form a fast diffusion path by reducing the diffusion activation energy. As a result, excessive grain growth is promoted and results in the formation of large grain. The fracture toughness of the MnO$_2$-doped 10Sc1CeSZ samples is reduced due to the amount of effective barrier to crack propagation decreased after thermal cycling.

The results showed that scandia-stabilized zirconia ceramics with no manganese impurity possessed better resistance to rapid thermal cycling degradation. This indicated that 10Sc1CeSZ can be used as electrolyte materials in SOFCs that are to be repeatedly and rapidly brought into high temperature operation in the fuel cell system

4. Conclusions
In this work, the microstructure and mechanical properties of the undoped and 1 wt% MnO$_2$-doped 10Sc1CeSZ ceramic samples were studied, before and after the samples being repeatedly heated for 30 cycles at 800 °C for 30 minutes with a heating rate of 10°C/min and 20°C/min. The results show that undoped 10Sc1CeSZ ceramic samples sintered at 1600 °C for 2 hours were fully dense, while the 1 wt% MnO$_2$-doped 10Sc1CeSZ ceramic samples only achieved ~92% of the theoretical density, before and

after thermal cycling. Undoped 10Sc1CeSZ ceramic samples showed higher Vickers hardness of 11.05 ± 0.34 GPa and fracture toughness ~ 2.9 MPa, with lower structural degradation after thermal cycling as compared to 1 wt% MnO_2-doped zirconia samples. Undoped 10Sc1CeSZ zirconia samples were able to suppress grain growth during thermal cycling and hence greater amount of grain boundaries that acts as effective barrier to the cleavage crack and resulted in higher fracture toughness. There were no significant changes in the mechanical properties for both samples thermal cycled at two different heating rates. The ability to withstand rapid thermal cycling in the zirconia ceramics is attributed to the large amount of grain boundaries that acted as impedance to dislocation movements and thus produced zirconia ceramics with high mechanical integrity

Acknowledgements

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