

Electrical and mechanical properties of cubic ZrO_2 stabilized with Sc_2O_3 and Y_2O_3

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It has been reported that Sc_2O_3 -doped ZrO_2 has the highest ionic conductivity among zirconia ceramics. The $x\text{mol}\%\text{Sc}_2\text{O}_3$ -added 3YSZ (abbr. $x\text{Sc3Y}$; $x = 0$ to 8) powders were prepared by homogeneous precipitation reaction using urea. A mixture of cubic and tetragonal phases was observed in every $x\text{Sc3Y}$ sample by XRD, and the amount of cubic phase increased with increasing Sc_2O_3 content. The ionic conductivity of $x\text{Sc3Y}$ exhibited a maximum, 0.244 S/cm at $x = 6$. Although the fracture toughness of $x\text{Sc3Y}$ decreased with an increase in x , $x\text{Sc3Y}$ samples were tougher than 8YSZ. The improvement in fracture toughness is due to the fine microstructure compared to 8YSZ and the difference in fracture mode. Sc_2O_3 -added 3YSZ should be applicable as an electrolyte for high performance solid oxide fuel cells (SOFC) replacing 8YSZ.

Key words: Yttria-zirconia, Scandia, Ionic conductivity, Fracture toughness, Solid oxide fuel cell.

Introduction

In a solid oxide fuel cell (SOFC), the electrolyte resistance is predominant in the electrical resistance of the entire cell. In order to improve the cell performance of planar-type SOFC, the resistance of the electrolyte should be reduced. There are two approaches for this improvement: to use a material of higher electrical conductivity and to reduce the thickness of the electrolyte and improve its mechanical strength. To improve mechanical properties, Ishizaki *et al.* [1] and Yamamoto *et al.* [2] studied composites of Y_2O_3 -stabilized ZrO_2 (YSZ) and Al_2O_3 . The electrical conductivity of the composites was 0.1 S/cm, and the mechanical strength was 1.4 times higher compared to 8YSZ itself. When using 8YSZ as an electrolyte, a serious problem is its low fracture toughness, that is its low resistance to crack propagation from thermal stresses under operation. In our laboratory, 8YSZ composites were made by distributing SiC whiskers coated with Al_2O_3 as a second phase, in order to improve the fracture toughness by a crack deflection mechanism, but this caused a degradation of ionic conductivity. The overall aim of our research is to develop an electrolyte having high ionic conductivity and excellent mechanical properties.

It is known that Sc_2O_3 -stabilized ZrO_2 (ScSZ) has the highest electrical conductivity in zirconia-based electrolytes. Many researchers try to explain this phenomenon on the radius of the dopant ion. Arachi *et al.* [3] have

shown that the ionic conductivity is high when the ionic radius of the dopant is close to that of the host cation (Zr^{4+}). The ionic radii of Zr^{4+} , Y^{3+} , and Sc^{3+} are 0.082, 0.095 and 0.084 nm, respectively. On the other hand, there are few reports of the mechanical properties of ScSZ, and another unknown factor is the dependence on composition and annealing time of phase transition.

3YSZ (3 mol% Y_2O_3 - ZrO_2) is known as a high toughness ceramics. In this study, Sc_2O_3 -added 3YSZ was prepared, and its electrical and mechanical properties were investigated.

Experimental

Sc_2O_3 was deposited in a 3YSZ powder (particle size: < 50 nm) suspension by homogeneous precipitation using urea, giving $x\text{mol}\%\text{Sc}_2\text{O}_3$ -added 3YSZ (abbr. $x\text{Sc3Y}$; $x = 0$ to 8) powders. The powders thus obtained were calcined at 850°C for 1h in air, pressed into pellets, and sintered at 1500°C for 2h in air. The powder composition was determined by energy dispersive X-ray fluorescence spectrometer (EDX). The crystalline phases of sintered $x\text{Sc3Y}$ were identified by powder X-ray diffraction (XRD). For electrical measurements, the sintered body was cut into a rectangular shape, and electrodes were set using platinum wire. The ionic conductivity was measured by a DC four terminal method in the temperature range from 300 to 1000°C under an open atmosphere. The fracture toughness and hardness were evaluated by the Vickers indentation fracture (IF) method. The microstructure of fracture surfaces was observed by scanning electron microscopy (SEM).

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Results and Discussion

Characterization of powders

From the results of EDX, the Sc/Zr molar ratio of $x\text{Sc}3\text{Y}$ powder obtained by homogeneous precipitation using urea was in agreement with the starting one. The powders consisted of tetragonal and monoclinic phases. After calcination at 850°C for 1h in air, the peaks from the monoclinic phase disappeared and the tetragonal phase remained. There was no change in particle size and state of the powder before and after calcination.

Crystalline phase of $x\text{Sc}3\text{Y}$

Sintered 3YSZ consisted of tetragonal and cubic phases. When Sc_2O_3 was added to 3YSZ from 3 to 8 mol%, the crystalline phase of the sintered body was mostly cubic phase (Fig. 1). The lattice constants, assuming that all $x\text{Sc}3\text{Y}$ samples consist of tetragonal phase, were calculated. The a and c axes decreased continuously, and the a/c ratio approached 1 with an increasing amount of Sc_2O_3 added (Fig. 2). These results suggest that 3YSZ became stable in the cubic state by Sc_2O_3

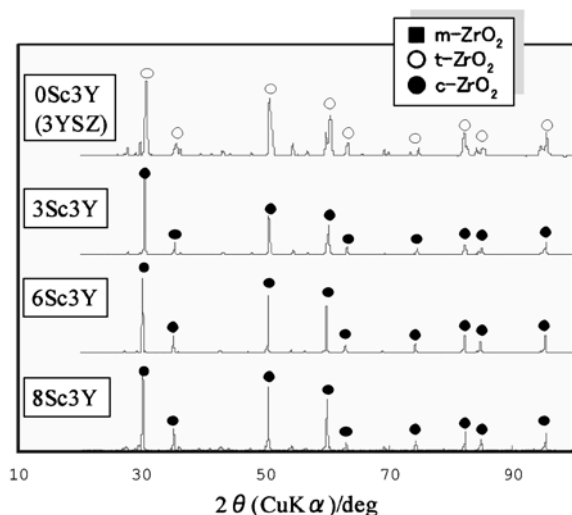


Fig. 1. X-ray diffraction patterns of $x\text{Sc}3\text{Y}$ (sintered at 1500°C for 2h in air).

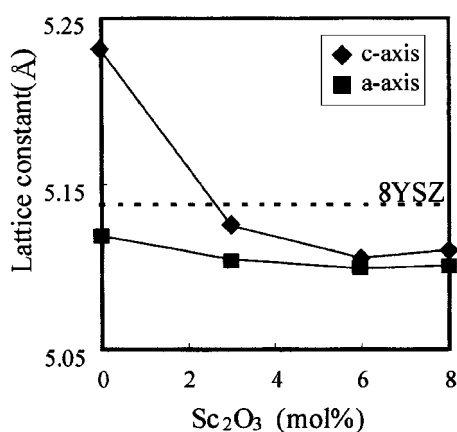


Fig. 2. Sc_2O_3 content dependence of lattice constant.

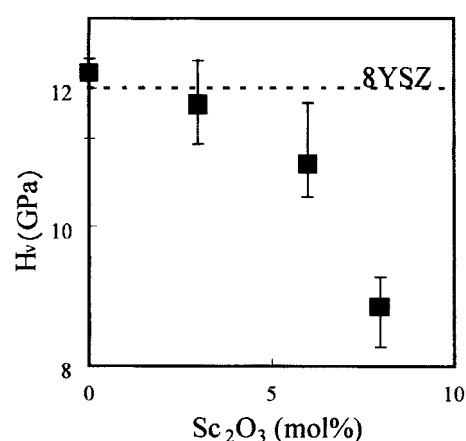


Fig. 3. Relationship between the Vickers hardness and Sc_2O_3 content.

addition, and Sc_2O_3 totally dissolved into the crystal lattice of ZrO_2 . Moreover, the values of a and c , when a/c was close to 1, were smaller than the lattice constant (0.5138 nm) of 8YSZ . This phenomenon can be explained as follows: the ionic radius of Sc^{3+} is smaller than that of Y^{3+} , so the crystal lattice of ZrO_2 is contracted by the addition of Sc.

Mechanical properties

The sintered density of $x\text{Sc}3\text{Y}$ decreased with an increase in Sc_2O_3 content. This result indicates that Sc_2O_3 addition retards the sintering of ZrO_2 . In $x\text{Sc}3\text{Y}$, the dopant ions, although the ionic radius differs greatly from each other (Sc^{3+} : 0.084 nm, Y^{3+} : 0.095 nm), exist in the crystal lattice of ZrO_2 . For this reason, it is thought that the sintering was suppressed owing to the difference in the diffusion rate of ions. Figure 3 shows the relationship between the Vickers hardness of $x\text{Sc}3\text{Y}$ and the Sc_2O_3 content. The Vickers hardness is known to depend strongly on density. Therefore, the fall of the hardness accompanied by an increase in the Sc_2O_3 content may be caused by a lowering of the density. The relationship between the fracture toughness and the Sc_2O_3 content is shown in Figure 4. When Sc_2O_3

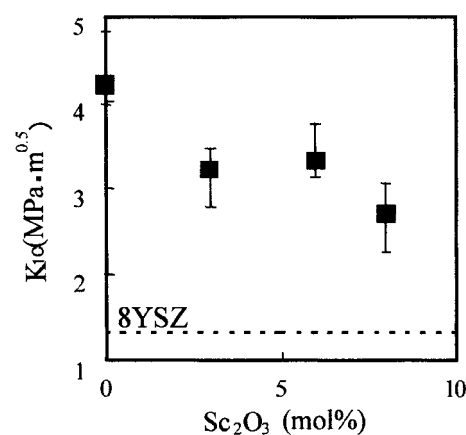


Fig. 4. Sc_2O_3 dependence of fracture toughness.

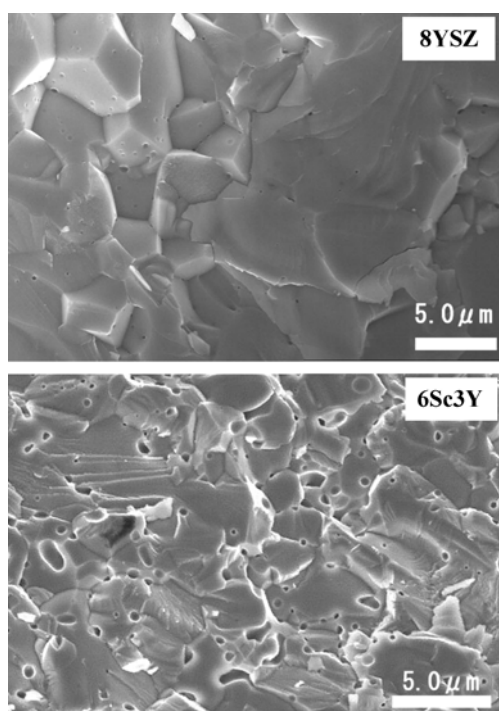


Fig. 5. Microstructure of fractures surface of 8YSZ and 6Sc3Y.

was added to 3YSZ, the fracture toughness fell. However, the toughness was higher than that of 8YSZ for every composition.

Microstructure of fracture surfaces

Figure 5 shows the microstructure of the fracture surfaces of 8YSZ and 6Sc3Y. Figure 6 shows the relationship between Sc_2O_3 content and grain size. The grain size of 3YSZ became large by adding Sc_2O_3 but was smaller than that of 8YSZ. The 3YSZ consisted of tetragonal and cubic phases, leading to a fine microstructure. When different crystalline phases exist, the diffusion of ions is retarded and grain growth is suppressed. Although xSc3Y consisted of mainly the cubic phase, the grain size was smaller than in 8YSZ. This

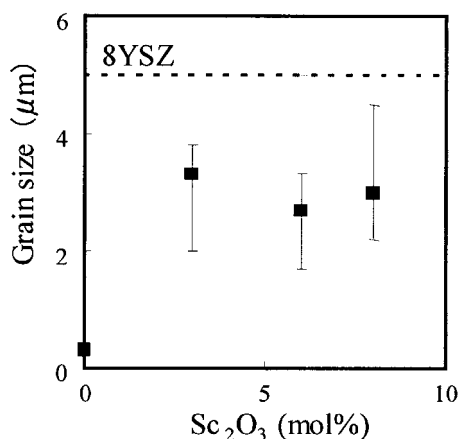


Fig. 6. Grain size of xSc3Y as a function of Sc_2O_3 content.

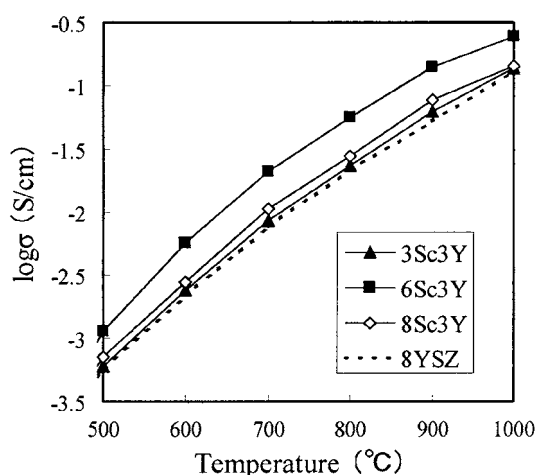


Fig. 7. Temperature dependence of electrical conductivity of xSc3Y.

may be based on the retardation of diffusion process described above. Although the fracture path was mainly intergranular in 8YSZ, 6Sc3Y mainly fractured within grains. As for xSc3Y, Sc and Y exist as impurities in pure ZrO_2 . If a second phase exists in the grain boundaries, the fracture toughness might be increased. In spite of the same cubic phase, it should be noted that xSc3Y has a higher toughness than 8YSZ, which may be related to the grain size and heterogeneity distribution of dopants at grain boundaries.

Electrical properties

The ionic conductivity of xSc3Y, 8YSZ, and 3YSZ is shown in Figure 7 as a function of temperature. The ionic conductivity of xSc3Y ($x=3, 6, 8$) was higher than that of 8YSZ. The σ at 1000°C is shown as a function of Sc_2O_3 content in Figure 8. At $x=6$, the ionic conductivity of xSc3Y became a maximum, and the value was 0.244 S/cm (2.4 times higher than in 8YSZ). In $x=8$, the ionic conductivity of xSc3Y fell. This may be due

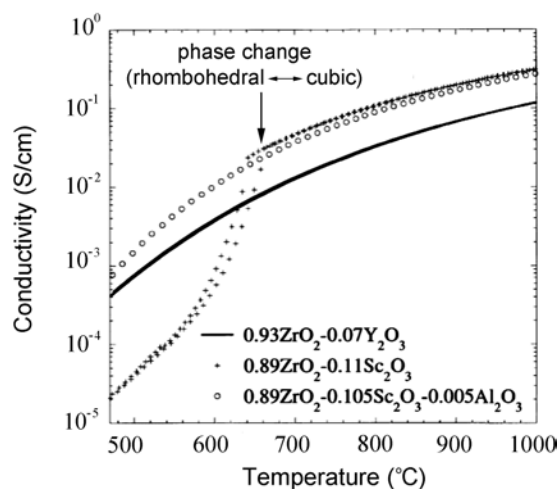


Fig. 8. The ionic conductivity of $0.92\text{ZrO}_2\text{-}0.08\text{Y}_2\text{O}_3$, $0.89\text{ZrO}_2\text{-}0.11\text{Sc}_2\text{O}_3$ and $0.89\text{ZrO}_2\text{-}0.105\text{Sc}_2\text{O}_3\text{-}0.005\text{Al}_2\text{O}_3$. (All samples are sintered at 1620°C .)

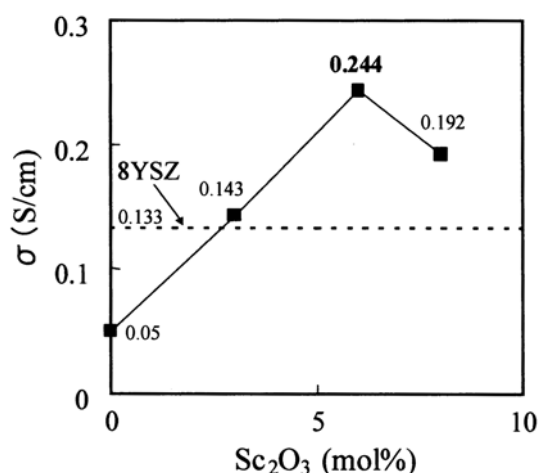


Fig. 9. Electrical conductivity of $x\text{Sc}_3\text{Y}$ at 1000°C as a function of Sc_2O_3 added.

to an association between dopants and oxygen vacancies. Since 8YSZ is cubic in the range of measurement temperature and does not cause a phase transition, the conductivity changed continuously with temperature. On the other hand, it has been reported in the Sc_2O_3 - ZrO_2 (ScSZ) system that the conductivity of ScSZ changes discontinuously because of a phase transition from cubic to a rhombohedral phase at about 600°C (Fig. 8) [4]. In the $x\text{Sc}_3\text{Y}$ system, however, the conductivity changed continuously over the measurement temperature (Fig. 7). This indicates that the phase transition did not occurred.

Conclusions

The electrical and mechanical properties of $x\text{mol}\%$ Sc_2O_3 -added 3YSZ ($x\text{Sc}_3\text{Y}$; $x=0$ to 8) were investigated. The $x\text{mol}\%$ Sc_2O_3 -added 3YSZ powder could be prepared by a homogeneous precipitation reaction using urea. The sintered $x\text{Sc}_3\text{Y}$ consisted of mainly the cubic phase, with a small amount of tetragonal phase. The amount of tetragonal phase decreased as the Sc_2O_3 content increased. When $x=6$, the ionic conductivity of $x\text{Sc}_3\text{Y}$ became a maximum, 0.244 S/cm (at 1000°C). The fracture toughness of $x\text{Sc}_3\text{Y}$ was high compared to 8YSZ. The grain size of $x\text{Sc}_3\text{Y}$ was smaller than in 8YSZ. In spite of the same cubic phase, as in 8YSZ, the high toughness may be related to a difference in grain size and dopant distribution.

References

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