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Thermal shock resistance and creep behavior of dispersion strengthened ion conductive zirconia ceramics

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We have already reported a favorable mechanical and electrical properties in 30 mol% of alumina added yttria full stabilized zirconia (8YSZ) ceramics. In the present study, thermal shock resistance and bending high temperature creep properties of this composite ionic conductor have been evaluated. Critical temperature difference at which mechanical strength shows sudden degradation, increased by 25 °C through alumina addition. In alumina added 8YSZ, creep resistance increased at steady-state creep region or strain rate of alumina added 8YSZ became half as large as that of 8YSZ without dispersoid, indicating an enhancement of creep resistance through alumina addition. The stress index n of alumina added 8YSZ was calculated to be 2, suggesting the grain-boundary sliding. No microstructural change such as crack formation was observed by SEM on the crept sample.

Key words: solid oxide fuel cell; ionic conductivity; composite; thermal shock resistance; creep

1. INTRODUCTION

Yttria stabilized zirconia (YSZ) is expected to be the most probable candidate of electrolyte for solid oxide fuel cell (SOFC) because it exhibits fast oxide ion conduction at high temperature without showing electric conduction. Especially, 8 mol% yttria stabilized zirconia (8YSZ) shows maximum ionic conductivity (2.0 X 10^{-2} Scm^{-1}, at 700°C) and chemical stability in a wide range of temperature[1]. However, 8YSZ is inferior to partially stabilized zirconia (PSZ) in mechanical strength while electrolyte of SOFC should play a role of separation wall[2,3]. Various works have been conducted concerning the improvement of mechanical strength in 8YSZ [4,5,6].

We have already fabricated an alumina/8YSZ composite showing a favorable mechanical strength as well as comparable ionic conductivity to conventional 8YSZ. When 8YSZ base powder compact added with 30 mol% of fine alumina, was sintered with rapid heating rate, mechanical strength of the composite ceramics became about twice as large as that of monolithic 8YSZ ceramics. Furthermore, ionic conductivity was almost maintained in spite of addition of electrically insulating material[7]. In our following study [8], internal residual stress arisen from the difference in thermal expansion coefficient between alumina and 8YSZ, have proved to contribute the toughening in addition to the load sharing and crack deflection owing to the alumina dispersion.

Since SOFC is operated at around 1000℃, it is needed to evaluate the mechanical characteristics concerning with the heat cycle and high temperature holding in addition to the usual short term mechanical and electric characteristics. In the present study, thermal shock resistance and high temperature bending creep properties of this composite ionic conductor have been evaluated.

2. EXPERIMENTAL

Alumina powder (Sumitomo Kagaku, AKP-30, 15,53, Kanto Kagaku; τ-alumina) was mixed into 8YSZ (Toshoh;TZ-8Y) with a predetermined ratio (0 % or 30 mol%). The mixture was wet blended with planetaly mill for 4 h using zirconia balls and ethanol. After dried, the powder mixture was sieved using stainless mesh (75μm) and was uniaxially pressed under 90 MPa in a stainless die (5 X 15 mm^2, inner size), followed by hydrostatic pressing with 135 MPa. The powder compacts were heated at the rate of 820°C/h or 200°C/h up to 1650 and were kept for 4h.

From the bulk composite test pieces were cut into rectangular bars of 2 X 4 X 12 X mm^3 for mechanical measurement.

The specimens were heated to desired temperatures for 30 min in a tube furnace and then quenched into ice water. Thermal quenching was conducted at temperatures from 20 to 300℃, which corresponded to thermal shock temperature differences (=ΔT). The thermally shocked specimens were dried before the residual strength measurement. Three to five samples were tested for each temperature difference.

Flexture creep tests were conducted in an air atmosphere at 1000℃ and constant stress of 60-160 MPa. The nominal applied stress and measured strain are maximum tensile surface stress and the strain, which were calculated by the midpoint displacement. After the thermal shock and creep experiment, fracture surface and tensile surface were observed by SEM, respectively.

3. RESULTS AND DISCUSSION

3.1 Thermal shock properties

Figure 1 shows the strength of 8YSZ added with alumina and 8YSZ without alumina as a function of thermal shock temperature difference (=ΔT). As we reported, starting strength or mechanical strength without thermal shock, of alumina added 8YSZ is almost twice as large as that of 8YSZ without dispersoid. The strength of both ceramics remains constant up to a certain ΔT and then drops suddenly at a point corresponding to the critical difference temperature(=ΔTc). This behavior is typical for brittle ceramics and is consistent with Hasselman's model[9].

The critical difference temperature of alumina added 8YSZ is larger than that of 8YSZ without dispersoid by 25℃, indicating higher thermal shock resistance. Furthermore, the residual mechanical strength of the former is also larger than the latter. The improved thermal shock resistance can be attributed to the presence of alumina phase in combination with the

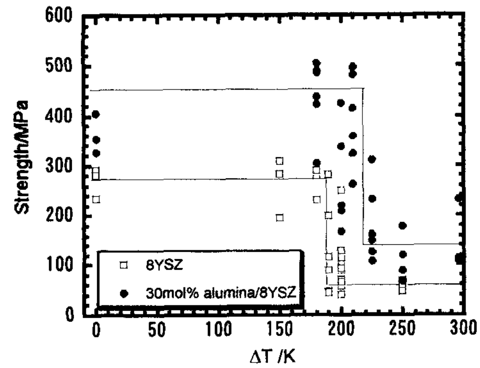

Fig.1 Thermal shock responce of 8YSZ and 30mol% alumina added 8YSZ

Table Mechanical Properties and calculated thermal shock resistance coefficient (R) of 8YSZ with and without alumina

	8YSZ	alumina/8YSZ
E/GPa	260	290
$\alpha/10^{-6}$	7.9	7.0
σ/MPa	250	480
R(calculated)	90	160
ΔTc(measured)	190	215

microstructural change in matrix.

The effect of microstructure on observed thermal shock behavior can be demonstrated by Hasselman's theory using the thermal shock resistance parameters, R, as,

$$R = \frac{\sigma(1-\nu)}{\alpha E} \quad (1)$$

where σ is the initial strength, E the Young's modulus, α the thermal expansion coefficient, and υ the Poisson ratio. The calculated R for 8YSZ with and without alumina are listed in Table.

Addition of alumina increases the initial strength and decreases the thermal expansion coefficient, which are favorable characteristics, while Young's modulus is also increase, counteracting to reduce the thermal shock resistance. The calculated R of 8YSZ without alumina is much smaller than the experimental value. This is probably attributed to the resistance to crack propagation while R parameter provides a measure of resistance to crack initiation.

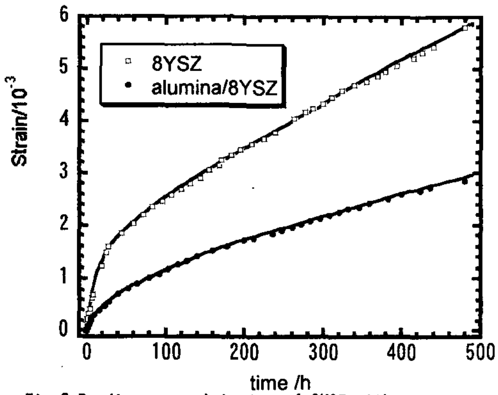

Fig. 2 Bending creep behavior of 8YSZ without dispersoid and 8YSZ with 30 mol% of alumina. (at 1000℃, under 120 MPa)

3.2 Creep properties

The bending creep curves of 8YSZ added with alumina and 8YSZ without dispersoid under 100MPa at 1000℃ are shown in Fig.2. In both cases, creep curve shows the steady state or minimum strain rate after the initial transient creep. The alumina added 8YSZ shows small strain rate half as large as that of 8YSZ without dispersoid, indicating a improved creep resistance.

Figure 3 shows the stress dependencies of creep rate of alumina added 8YSZ. Stress dependency of a steady-state creep rate of polycrystalline ceramics is generally expressed by

$$\frac{d\varepsilon}{dt} = C\sigma^n \qquad (2)$$

where dε/dt is the steady state creep rate, C a constant, σ the applied stress, and n the stress exponent of creep rate, which can be determined from the slope of Fig.3. The plots of the alumina added 8YSZ followed this relation well when n = 2.2. The stress exponent of single phase ceramics is known to typically range from 1 to 2, with values near 2 being controlled by grain-boundary sliding. From the SEM observation on crept sample, microstructural change such as cavitation can not be identify.

Ohji et al.[10] reported that the improvement of creep resistance for the Al_2O_3/SiC nanocomposite was due to the pinning effect of the intergranular SiC particle, because the intergranular SiC particles rotated and plunged into the Al_2O_3 grains during the grain-boundary sliding.

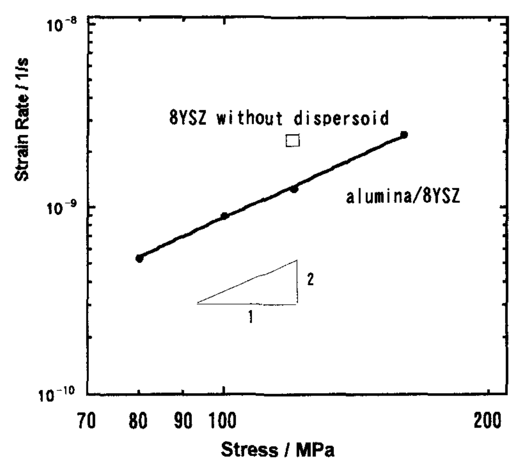

Fig.3 Stress dependency of steady-state creep rate for 8YSZ with 30 mol% of alumina.

In this nanocomposite, however, creep rate was reduced by almost 3 order of magnitude, while the reduction ratio is one-half in the present study.

The difference in creep resistance improvement can be explained by taking into account of the grain size. We have previously reported that the alumina addition has a role in suppressing grain growth of matrix zirconia [11]. Grain size dependence of creep rate is known to be negative even in composite material [12]. The addition of alumina impedes the grain-boundary sliding, while grain side reduction facilitate the grain-boundary sliding, resulting in the slight improvement of creep resistance.

4.CONCLUSIONS

Thermal shock resistance and bending high temperature creep properties of this composite ionic conductor have been evaluated. Critical temperature difference at which mechanical strength shows sudden degradation, increased by 25C through alumina addition. In alumina added 8YSZ, creep resistance increased at constant creep region or strain rate of alumina added 8YSZ became half as large as that of 8YSZ without dispersoid, indicating an enhancement of creep resistance through alumina addition. The stress index n of alumina added 8YSZ was calculated to be 2, suggesting grain-boundary sliding creep. No microstructural change such as crack formation was observed by SEM on the creep strained sample.

Acknowledgements

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