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Effect of electric field on 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, bending high temperature creep properties of this composite ionic conductor have been evaluated. And the effect of electric field on such composite was investigated. 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 (at 1000°C under 100 MPa), indicating an enhancement of creep resistance through alumina addition. The stress index n of alumina-added 8YSZ was calculated to be 2.0, suggesting the grain-boundary sliding. There was a tendency that strain rate was facilitated by applying the electric field with compressive side positive.
Key words: solid oxide fuel cell; ionic conductivity; composite; creep

1. INTRODUCTION

Since yttria stabilized zirconia (YSZ) exhibits fast oxide ion conduction at high temperature without showing electric conduction, it is expected to be the most probable candidate of electrolyte for solid oxide fuel cell (SOFC). Especially, 8 mol% yttria stabilized zirconia (8YSZ) shows faborable ionic conductivity and chemical stability in a wide range of temperature[1]. However, 8YSZ is inferior to partially stabilized zirconia (PSZ) such as 3 mol% yttria stabilized zirconia (3YSZ) in mechanical strength while electrolyte of SOFC should play a role of separation wall[2,3].

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 the addition of electrically insulating material[4]. In our following study [5], 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 high temperature holding in addition to the usual short term mechanical and electric characteristics. In the present study, high temperature bending creep properties of this composite ionic conductor have been evaluated. And the effect of electric field on such property was investigated.

2. 2. EXPERIMENTAL

Alumina powder (Sumitomo Kagaku, AKP-30) 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 (75mm) 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 up to 1650 and were kept for 4h. From the bulk composite test pieces were cut into rectangular bars of

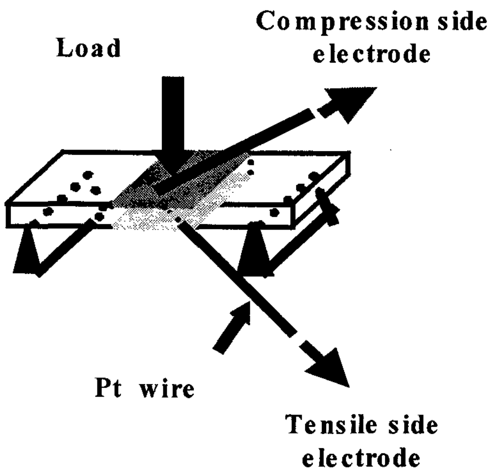

Fig.1 Sample setup of bending creep test under electric field

2 X 4 X 12 X mm^3 for high temperature creep measurement.

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.

In order to investigate the effect of electric field on creep deformation, platinum electrodes (4mm span) were sputtered as shown in Fig. 1. The applied voltage was 11 V (=55V/cm) either from compression side to tensile side (compression side positive) or tensile side to compression side (tensile side positive)

3. RESULTS AND DISCUSSION

3.1 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 strain rates at the steady state were calculated from the slope of both profiles. 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

$$\frac{d\varepsilon}{dt} = C\sigma^n$$

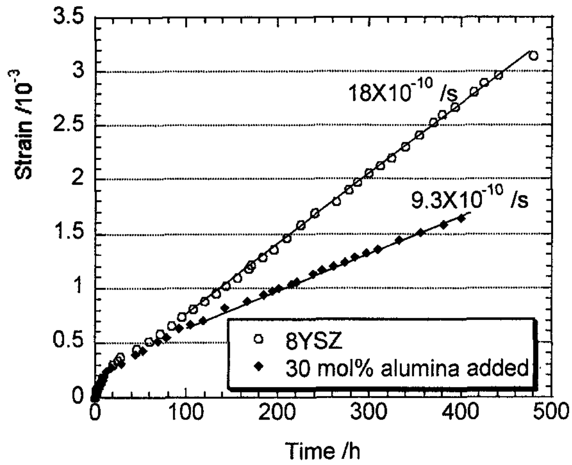

Fig.2 Creep behavior of 8YSZ and 30 mol% alumina added 8YSZ at 1000C under 100MPa

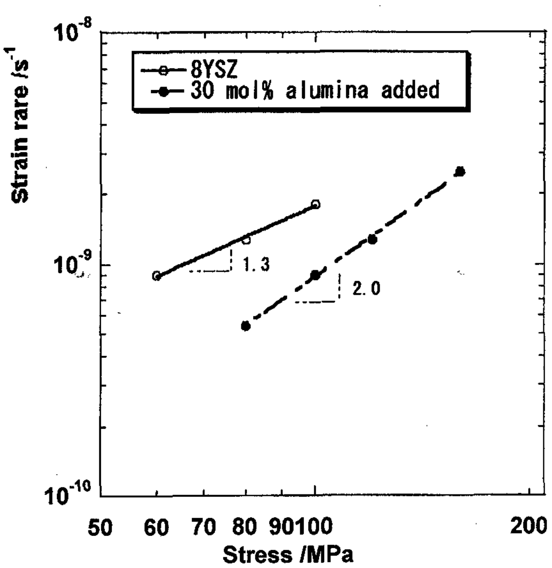

Fig.3 Relationship between ln(σ) and ln($d\varepsilon/dt$) in 8YSZ and alumina added 8YSZ at 1000C.

where $d\varepsilon/dt$ 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 8YSZ and alumina-added 8YSZ followed this relation well when n=1.3 and n = 2.0, respectively. The stress exponent of single phase ceramics is known to typically range from 1 to 2. From the SEM observation on crept sample, microstructural change such as cavitation or void cannot be identified.

It is usually accepted that grain boundary sliding is dominant which n =1 and inner grain deformation is the dominant process when n >3. It can be said that the creep mechanism can be described by the grain boundary sliding while the contribution of the inner

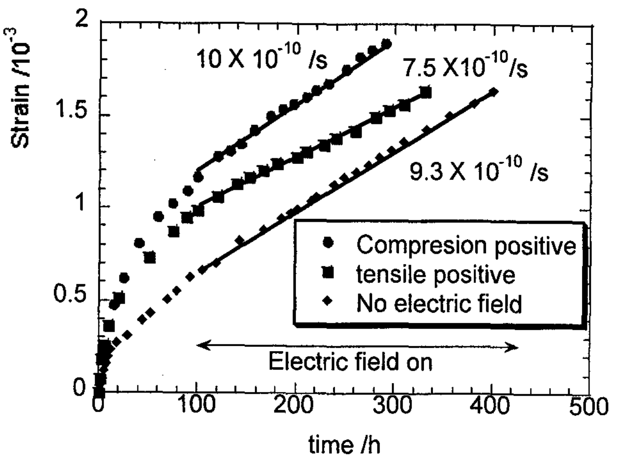

Fig.4 Effect of electric field (55 V/cm) on creep strain of 30 mol% alumina added 8YSZ

grain deformation might appear by adding alumina particle.

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 [6]. Grain size dependence of creep rate is known to be negative even in composite material [7]. The addition of alumina impedes the grain-boundary sliding, while grain size reduction facilitate the grain-boundary sliding, resulting in the slight improvement of creep resistance.

In the monolithic 8YSZ, sliding occurs much easier along grain boundary than inner grain. On incorporating alumina, the sliding along the grain boundary is inhibited. As a result, inner grain sliding would contribute the creep property, then the stress index increased to 2.0 which is between grain boundary dominant value (1) and inner grain one (3).

On such alumina-added sample of which creep resistance was improved, effect of electric field on creep property was evaluated. Electric field was applied either from compression side to tensile one (compression side positive) or from tensile side to compression one (tensile side positive) after holding 100 h under a constant bending stress, at which the creep property has comes to the steady state. The results are shown in Fig.4. Profile of transition creep is different between samples but the steady state creep rates show similar values. Furthermore there is a tendency that the creep rate increases with electric field compression side positive and decreases with tensile side positive compared with that of no electric field.

In order to confirm that the electric field dependency does not reflect the difference between

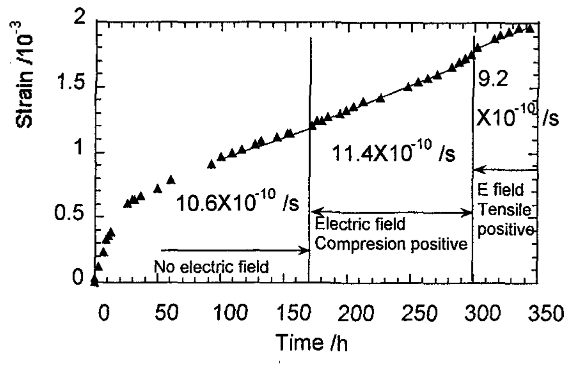

Fig.5 Effect of electric field on creep behavior of 30 mol% alumina added 8YSZ

samples, applied electric field was turned in the opposite way on the same samples. In this experiment creep rate of without electric field was calculated from the profile between 100 h to 170 h and the rate with electric field compression side down was calculated profile between 170 h to 300 h, to be 10.6X10^{-10}, and 11.4X10^{-10}, respectively. There is also a tendency that the creep rate increase with electric field compression side positive and decreases with tensile side negative.

In oxide ceramics, the diffusivities of the cations and anions are generally very different, then the creep rate is controlled by the diffusion rate of the slowest species along its fastest transport path. In fluorite-type oxide, such as stabilized zirconia, the cation diffusivities are several orders of magnitude lower than the oxide diffusivites[8-9]. As a result, diffusional creep in yttria-stabilized zirconia (YSZ) should be rate limited by cation diffusion either through the lattice or along the grain boundaries.

In the present case, the grain-boundary sliding was the dominant process for creep deformation from the stress exponent in Fig.3. Therefore, cation diffusion along the grain boundaries is the rate limiting process if lattice deformation can be negligible.

4.CONCLUSIONS

Bending high temperature creep properties of this composite ionic conductor have been evaluated. The strain rate of alumina-added 8YSZ at constant creep region 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. There was a tendency that strain rate was facilitated by applying the electric field with compressive side positive.

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