OXYGEN PARTIAL PRESSURE DEPENDENCE OF CREEP FOR YTTRIA-DOPED CERIA CERAMICS

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ABSTRACT

Rare earth-doped ceria ceramics are potential candidates for an electrolyte in medium-temperature solid oxide fuel cells (SOFC). However, the mechanical properties under the practical working environments of SOFCs have not been fully investigated for CeO₂ based electrolytes. In this study, creep behaviors of CeO₂-YO₁.₅ were investigated at stresses of 20-39 MPa and temperatures of 1045 to 1125°C under controlled oxygen partial pressure (PO₂). The stress exponent n=0.96 and the activation energy Q=264 kJ/mol of creep rate were obtained experimentally in air. Because this value is much higher than that for anion diffusion in this material, it was concluded that creep is controlled by a cation diffusion mechanism. It was found that the oxygen partial pressure dependence of the steady-state strain rate has a peak at PO₂=10⁻⁴ atm and the profile is similar to electrical conductivity.

INTRODUCTION

The most widely used electrolyte in solid oxide fuel cells (SOFCs) is yttria-stabilised zirconia (YSZ). However, the cells must operate at temperatures between 900° and 1000° to achieve acceptable efficiencies and are limited in the choice of electrode and interconnects materials at this temperature range. Rare earth-doped ceria is a possible candidate as an electrolyte and in medium-temperature (600°-800°C) SOFCs. Doped ceria is, however, partially reduced under high-temperature reducing atmospheres like the fuel environment in SOFCs. This effect causes expansion of the crystal lattice and doped ceria will show a relative expansion at the reducing side. This phenomenon leads to the internal stress in the materials. The magnitude of this stress was estimated by Atkinson. He found that a relatively high stress generates under practical SOFC operating conditions (1). Yasuda and Hishimura reported a similar interesting analysis (2). For this reason, it is important to investigate the mechanical properties of the component materials of SOFCs to design and fabricate a unit cell and stack.

The mechanical properties of doped ceria have been reported by several researchers (3).
Most of the data was taken on Gd-doped CeO$_2$ samples at room temperature or a high
temperature in air. The mechanical properties (strength, creep behavior, toughness, etc.)
for rare earth-doped ceria have not been studied enough for practical SOFC operating
conditions, especially creep behavior of pure or doped ceria.

In this study, creep behavior of (CeO$_2$)$_{0.8}$(YO$_{1.5}$)$_{0.2}$ (20YDC) was investigated at 20–
39 MPa and 1045°–1125°C to obtain the stress exponent and activation energy for creep
and to estimate creep rate in SOFC operating conditions. The creep behavior was also
investigated by changing oxygen partial pressure from 0.21 to 10$^{-16}$ atm. The relationship
between defect chemistry and creep mechanism in doped ceria is discussed.

**EXPERIMENTAL**

**Specimen Preparation**

A (CeO$_2$)$_{0.8}$(YO$_{1.5}$)$_{0.2}$ sample was synthesized by the coprecipitation method from CeO$_2$
(99.99%, Nihon Yttrium Corp) and Y$_2$O$_3$ (99.99%, Nihon Yttrium Corp). The precip­
itation was calcined at 900°C for 5 h in air. The X-ray diffraction measurement showed
that the powder was a single phase of fluorite structure. The powder was then ball milled
for 24 h in distilled water. After drying, the powder was consolidated by isostatic
pressing at 1.4 ton/cm$^2$ and sintered at 1500°C for 6 h in air. The sintered bar was cut and
polished to yield a creep specimen of approximately 37 x 4 x 1 mm.

After polishing, the specimen was annealed at 1000°C for 3 h to remove induced residual
stress. The relative density of the specimen was greater than 95% of theoretical value and
the average grain size of the specimen was about 4.4 μm.

**Creep Test Equipment**

Creep behavior was observed by a four-point bending creep test at constant load in air. A
schematic illustration of this creep test machine is shown in Figure 1. The loading points
and supporting points were made of SiC because of its mechanical stability at high
temperatures. The deflection of the specimen was measured using linear variable
differential transformer (LVDT) with Al$_2$O$_3$ rod contacting the center of the bottom of the
specimen in the furnace and the load was measured by a load cell. The creep test was
conducted at stresses of 20–39 MPa and temperatures between 1045° and 1125°C.

Scanning electron microscopy (SEM) examination of the sample was performed before
and after the creep tests.

**RESULTS AND DISCUSSION**

Typical creep curves at 39 MPa are shown in Figure 1. Just after applying the load, the
elastic deformation followed by transition creep was observed. Apparent steady-state
creep was observed after a long time. The steady state-strain rate was estimated from the
slope of Figure 1. The steady-state strain rate, $\dot{\varepsilon}$, depends on absolute temperature, T, and
applied stress, $\sigma$, and is generally described by Eq. [1]:

\[ \dot{\varepsilon} = C \sigma^n \exp \left( -\frac{Q}{RT} \right) \]

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\[ \dot{\varepsilon} = A\sigma^n \exp\left(-\frac{Q}{RT}\right) \]  

where \( n \) is the stress exponent for creep, \( Q \) is activation energy for creep, \( R \) is the universal gas constant, and \( A \) is a parameter that depends on the material and test conditions. The experimental value of \( n \) and \( Q \) can be compared with theoretical values and combined with the microstructural observations to determine the rate-controlling deformation mechanism.

The stress dependence of strain rate for 20 YDC at 1100°C in air is shown in Figure 3. The stress exponent, \( n \), was calculated to be 0.96 ± 0.1 from this figure. Furthermore, it is revealed from SEM observation that the grain structure does not change during deformation. These results indicate that creep was controlled by a diffusion mechanism. The activation energy for creep rate of 20 YDC at 39 MPa is estimated to be about 264 kJ/mol from the temperature dependence of steady-state strain rate, as shown in Figure 4. This value is almost the same as that previously reported on undoped ceria (314 kJ/mol) under similar conditions (4). Because the activation energy for anion diffusion in 20 YDC is much lower (about 77 kJ/mol) than this activation energy, it is considered that creep was controlled by cation diffusion mechanism.

The steady-state creep rate of 20 YDC is much smaller than that of undoped ceria at the same conditions (4). The effect of solute ion concentration on cation diffusion coefficient (creep rate) was reported on YSZ by Wakai and Nagano (5). They found a great difference in cation diffusion coefficient between less than 6 mol% Y2O3 doped zirconia (about \( 10^{-15} \) m²sec⁻¹) and more than 8 mol% Y2O3 doped zirconia (about \( 10^{-17} \) m²sec⁻¹). The difference in strain rate between CeO₂ and 20 YDC, which have the same crystal structure as YSZ, was probably caused by the same phenomenon. The magnitude of the strain rate of 20 YDC was very small (about \( 10^{-10} \) s⁻¹) even in the measured temperature range. So, it can be concluded that the effect of creep behavior on the strength of 20 YDC at practical operating temperatures (600°-800°C) is very little.

However, according to the report by Poluboyarinov et al. on the creep of ceria, the strain rate depended on the stoichiometry of the oxide (6). They found that the strain rate of CeO₁.₉ was faster than that of stoichiometric CeO₂, and the stress exponent and activation energy varied depending on the stoichiometry. So there is a possibility of change in creep behavior of 20 YDC in reducing atmospheres like the fuel environment in SOFCs. We are now investigating the creep behavior of 20 YDC in reducing atmospheres.

The oxygen partial pressure dependence of creep rate on 20 YDC at 1100°C is shown in Figure 5. The activation energy of strain rate under the constant oxygen non-stoichiometry (\( \delta = 0.085 \)), which is estimated from the data of thermal gravity by Otake et al. (7), is estimated to be 316 kJ/mol at 39 MPa. This value is almost the same order of magnitude as that obtained in air. This result leads to the conclusion that the creep is controlled by a cation diffusion mechanism in reduced atmosphere. As shown in Figure 5, the creep rate increases with decreasing oxygen partial pressure until \( P_{O_2} = 10^{-14} \) atm. The creep rate shows a peak at that pressure, and then decreases at lower \( P_{O_2} \) range. The peak position of creep rate is very close to that of total electrical conductivity of 20 YDC. This result strongly suggests that the creep mechanism depends on the oxygen partial pressure.
Furthermore, it is revealed that the creep due to slow cation diffusion can be related to the first oxygen diffusion process in this material.

According to the preliminary consideration of defect equilibrium in 20 YDC, the concentration of cerium vacancy decreases with decreasing oxygen partial pressure below PO2<10\(^{-10}\) atm, and the concentration of interstitial cerium increases below that oxygen partial pressure. The creep rate increase below 10\(^{-10}\)atm can be understood by changing the dominant process of creep from cerium vacancy to interstitial cerium. However, the decrease of creep rate at lower oxygen partial pressure can not be explained by simple defect models. This is quite similar to the case of the oxygen partial pressure dependence of electrical conductivity in doped ceria system. In the case of electrical conductivity, the complex defect structure or oxygen ordering models are considered to understand the experimental results. Because the profile of oxygen partial pressure dependence of creep rate is similar to that of electrical conductivity, it can be concluded that the structural change at lower oxygen partial pressure range will affect not only the electrical properties but also the mechanical properties in YDC.

**SUMMARY**

The creep property of \((\text{CeO}_2)_{0.8}(\text{YO}_1.5)_{0.2}\) was investigated at stresses of 20–39 MPa and temperatures of 1045\(^\circ\)C to 1125\(^\circ\)C under controlled oxygen partial pressure. Because the stress exponent n=0.96 and the activation energy \(Q\approx264\) kJ/mol of creep rate were experimentally obtained in air, it was considered that creep was controlled by a cation diffusion mechanism. It was found that the steady-state strain rate depends on oxygen partial pressure and shows a peak at PO2=10\(^{-14}\)atm. The origin of creep rate decrease at lower PO2 was connected with electrical conductivity decrease at the PO2 range in YDC.

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Figure 1. Schematic illustration of the creep test chamber. The oxygen partial pressure was measured by a ZrO₂-sensor.

Figure 2. A typical temperature dependence of creep curves.

Figure 3. Stress dependence of strain rate for 20 YDC at 1100°C.
Figure 4. Temperature dependence of strain rate for 20 YDC at 1100°C, 39 MPa.

Figure 5. PO$_2$ dependence of steady-state strain rate of 20 YDC at 1100°C, 39 MPa.

264 ± 11 kJ/mol