

Short communication

Creep resistance comparison of two solid oxygen fuel cell electrolytes with the fluorite structure: cubic zirconia and doped-ceria

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Cubic zirconia and doped-ceria are oxygen conducting membranes that are used as electrolytes in solid oxide fuel cells (SOFCs) [1–5]. In order for cubic zirconia and doped-ceria to be used as electrolytes in SOFCs they must possess certain mechanical requirements, which include; adequate room temperature fracture toughness and high-temperature creep resistance. Investigation of high-temperature creep is important for the following reasons: (1) ascertain about dimensional stability at temperature under load, (2) fabrication into complex shapes that may be required in certain applications will most likely be conducted at elevated temperature and (3) determine diffusion information about the slowest-moving species. Information about the slowest-moving species is important because, both sintering and grain growth are also controlled by the slower-moving species.

The creep behavior of cubic zirconia [6–10] and doped-ceria [11] has been investigated in the past. It has been shown that cubic zirconia tested over the grain size range between 1 and 20 μm deforms by a grain boundary sliding mechanism accommodated by cation (Zr^{4+}) lattice diffusion. Over the aliovalent cation (Y^{3+} or Ca^{2+} or Sc^{3+}) doping range of 6–18 mol% the creep rate was independent of oxygen partial pressure. For the case of doped-ceria (10 mol% Gd^{3+}) [11] tested at a grain size of about 1 μm it was observed that it also deforms by grain boundary sliding accommodated by cation (Ce^{4+}) lattice diffusion. The creep rate for doped-ceria was also independent of oxygen partial pressure.

It has been observed for many metals and structural ceramics of the same structural group (i.e. face-centered cubic) whose creep deformation is controlled by the same

mechanism, that they will exhibit similar creep resistance when normalized for impurity concentration, oxygen partial pressure (for the case oxides), grain size and temperature [12–17]. Both cubic zirconia and doped-ceria have the fluorite crystal structure, which can be thought of as a face-centered cubic stacking of the metal ions with the oxygen ions occupying the tetrahedral interstices within the metal ion frame work [12].

It is the purpose of this note to determine if polycrystalline cubic zirconia and doped-ceria will exhibit similar creep resistance when normalized for impurity concentration, oxygen partial pressure, grain size and temperature. If such a trend exists this may be useful in predicting the creep behavior of other of new solid oxygen conducting electrolytes if the creep behavior of one only material in that class is well characterized, without testing all the materials of similar structure, as long as some basic information about the material's physical properties (i.e. melting temperature) are known.

The creep behavior of a polycrystalline oxide in general can be described by the following equation [18–20]:

$$\dot{\epsilon} = A\sigma^n L^{-p} [B] P(\text{O}_2)^m \exp\left(-\frac{Q_c}{RT}\right) \quad (1)$$

where $\dot{\epsilon}$ is the steady-state creep rate, σ the applied stress, n the stress exponent, L the grain size, p the grain size exponent, $[B]$ the concentration of the rate-controlling defect, $P(\text{O}_2)$ the oxygen partial pressure, m the oxygen partial pressure exponent, Q_c the activation energy for creep, A the constant, T the absolute temperature and R is the gas constant. From Eq. (1), it is observed that in order to compare the creep resistance of cubic zirconia and doped-ceria tested at different stresses, grain sizes, impurity concentrations, and oxygen partial pressures at various temperatures the creep parameters; n , p , $[B]$, m , Q_c and A for both must be known.

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The creep parameters for cubic zirconia taken from several sources [6–10] are as follows: $n \approx 1$, $p \approx 2$, $m \approx 0$ and $Q_c \approx 460$ kJ/mol [9]. The creep data for doped-ceria are as follows: $n \approx 1$, $m \approx 0$ and $Q_c \approx 480$ kJ/mol [11]. Using this information with following assumptions the creep resistance of cubic zirconia and doped-ceria can be compared to determine if the normalized creep rates are similar.

The first assumption is that p in Eq. (1) for doped-ceria is ≈ 2 . Since, doped-ceria was tested at only one grain size there is not enough data to determine p . However, it is known that when the activation energy for creep is normalized with respect to the absolute melting temperature of the material, T_m , the ratio of Q_c/RT_m for materials of a similar structural group is about the same [12,21]. This result implies that the same diffusion mechanism (lattice or grain boundary) is operative in all materials of that structural group. For cubic zirconia $Q_c/RT_m \approx 0.19$ and for doped-ceria $Q_c/RT_m \approx 0.20$. These two values are in excellent agreement, suggesting that the same diffusion mechanism is operative in both. It was been experimentally shown that $p \approx 2$ (lattice diffusion) for cubic zirconia [6–10]. Thus, using $p \approx 2$ for doped-ceria to normalize the creep data is justified. The second assumption is that $[B]$ in Eq. (1) for both cubic zirconia and doped-ceria is about the same. In the temperature and oxygen partial pressure range tested $[B]$ is primarily a function of the aliovalent cation dopant concentration for both cubic zirconia and doped-ceria [6–11]. Cubic zirconia has an aliovalent cation concentration ≈ 6 –18 mol%, while doped-ceria has an aliovalent cation concentration ≈ 10 mol%. Thus, they have about the same aliovalent cation dopant concentration and hence, $[B]$ for the two materials should be similar, justifying the second assumption. The third assumption is that the constant A in Eq. (1) for both materials is the same. This is very reasonable since, A for a grain boundary sliding

accommodated by diffusion mechanism is primarily a function of grain shape and type of loading (i.e. compression versus shear) [13–19]. Since, both materials exhibit equiaxed grains, deform by the same mechanism and all tests were conducted under compression this assumption is justified.

The normalized creep resistance for cubic zirconia and doped-ceria are shown in Fig. 1. In addition, the normalized creep resistance for a potential new solid oxygen conducting electrolyte for SOFCs, fine-grained $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ (perovskite structure) is also shown in Fig. 1. The creep parameters for $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ are as follows: $n \approx 1$, $p \approx 2$, $m \approx 0$ and $Q_c \approx 520$ kJ/mol [8,9,22,23]. From Fig. 1, several important points are noted. Firstly, the creep data after compensation for cubic zirconia from different sources are in excellent agreement with each other. Secondly, the normalized creep rates for cubic zirconia and doped-ceria are in good agreement with each other. They are within a factor of about 5. This is well within the range exhibited by polycrystalline metals [16] and structural ceramics [15,17]. Thirdly, at a given value of applied stress the compensated steady-state creep rate for fine-grained $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ is at least between 1000 times faster than that for cubic zirconia and doped-ceria.

The results reveal that the creep resistance of the solid oxygen conducting materials with the fluorite structure, cubic zirconia and doped-ceria, when normalized by grain sizes, impurity concentrations, and oxygen partial pressures and temperatures are similar. This observation is in agreement with the behavior exhibited by metals and structural ceramics. In addition, the new potential solid state oxygen conducting electrolyte, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ (perovskite) will not be as creep resistance as either cubic zirconia or doped-ceria.

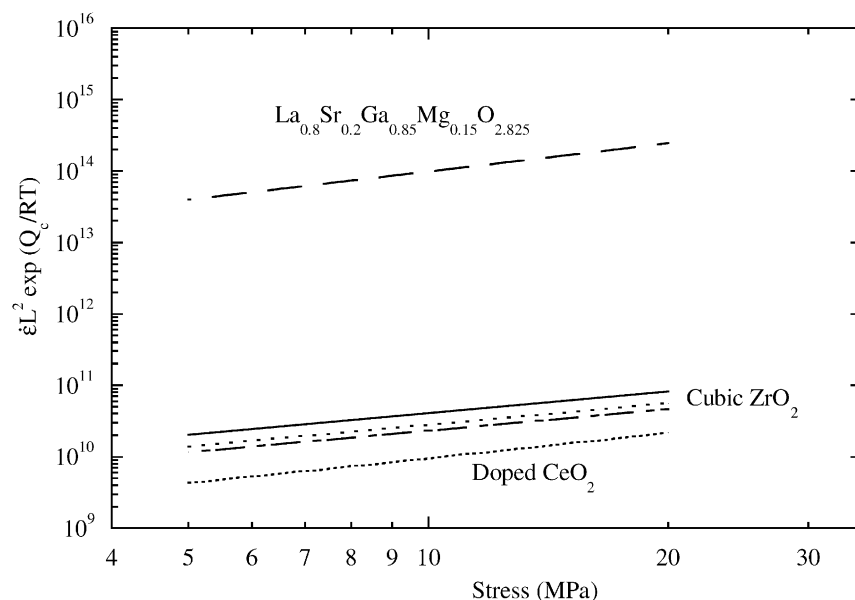


Fig. 1. Grain size and temperature compensated steady-state creep rate vs. applied stress for cubic zirconia, doped-ceria and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ [9].

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