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Intrinsic Creep Resistance of Two Solid Oxygen Fuel Cell Electrolytes: Cubic Zirconia Versus Doped Lanthanum Gallate

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Intrinsic Creep Resistance of Two Solid Oxygen Fuel Cell Electrolytes: Cubic Zirconia Versus Doped Lanthanum Gallate

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Sensors and Electron Devices Directorate

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Abstract

Knowledge of the creep parameters for cubic zirconia and doped lanthanum gallate allowed for a determination of the intrinsic creep resistance of each material in the temperature range from 800 to 1000 °C, where they are to be utilized as electrolytes in solid oxygen fuel cells. The results revealed that the intrinsic creep resistance of cubic zirconia is much higher than that of doped lanthanum gallate. This is most likely a result of their different crystal structures.

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Introduction

For a material to be used as an electrolyte in solid oxygen fuel cells (SOFCs), there are many important primary requirements. These include (i) high ionic conductivity, (ii) chemical stability with cell components, and (iii) thermal expansion match with that of the cell components [1–4]. In addition, there are some secondary mechanical property requirements such as good high-temperature creep resistance and room-temperature fracture toughness. Investigation of the high-temperature creep properties is important to gain information about the dimensional stability of the material at temperature under load.

It was previously shown at 1300 °C that the creep resistance of cubic zirconia was greater than that of doped lanthanum gallate ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ (LSGM-2015)) [5]. I wanted to determine if this comparison would hold in the temperature range from 800 to 1000 °C, where these materials are to be used as electrolytes in SOFCs. Thus, this report presents the first comparison of the intrinsic creep resistance of cubic zirconia versus LSGM-2015 over this temperature range.

The creep behavior of a polycrystalline oxide in general can be described by the following equation [6–8]:

$$\dot{\epsilon} = A \sigma^n L^{-p} P(\text{O}_2)^m \exp(-Q_c/RT) , \quad (1)$$

where $\dot{\epsilon}$ is the steady-state creep rate, σ is the applied stress, n is the stress exponent, L is the grain size, p is the grain size exponent, $P(\text{O}_2)$ is the oxygen partial pressure, m is the oxygen partial pressure exponent, Q_c is the activation energy for creep, A is a constant, T is the absolute temperature, and R is the gas constant.

What we mean by intrinsic creep resistance is that the creep rate is a function only of the material's intrinsic properties (i.e., modulus) and not a function of external variables such as grain size, oxygen partial pressure, etc. For example, from equation (1) we see that for the same material of different grain sizes the creep rate will be different if $p \neq 0$. Thus, to obtain the intrinsic creep resistance of the material, the parameter p must be known for that material. Consequently, from equation (1) we see that to compare the intrinsic creep resistance of different materials tested at different stresses, grain sizes, and oxygen partial pressures at various temperatures, we must know the creep parameters n , p , m , Q_c , and A for each material.

Determining Creep Resistance

The creep parameters for cubic zirconia [9–13] from several sources are summarized in table 1 along with those for $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ [5,14]. I would like to make several points from table 1. First, both materials exhibit a fine grain size (the linear intercept grain size is $\leq 20\mu\text{m}$). Second, the steady-state creep rate varies approximately inversely with the grain size, and is approximately squared for both cubic zirconia and LSGM-2015. Third, the stress exponent is close to unity for both materials. These three points suggest that both materials deform by the same mechanism: either diffusional creep or grain boundary sliding accommodated by diffusion [15–18]. Finally, the steady-state creep rate is independent of oxygen partial pressure ($m = 0$) for both materials.

Using the information from table 1 with the two assumptions below, the intrinsic creep resistance of cubic zirconia and LSGM-2015 in the temperature range from 800 to 1000 °C can be compared to determine which is the most creep-resistant. The first assumption is that the constant A in equation (1) is the same for both materials. This is very reasonable since A for either a diffusional creep or grain boundary sliding accommodated by diffusion mechanism is primarily a function of grain shape and type of loading (i.e., compression versus shear) [15–18]. This assumption is justified since both materials exhibit equiaxed grains, deform by the same mechanism, and all tests were conducted under compression. The second assumption is that the same mechanism that controls deformation (i.e., creep parameters) in the temperature range shown in table 1 remains the same in the temperature range from 800 to 1000 °C. Without experimental data in this temperature range, this assumption cannot be confirmed. To obtain creep data in this temperature range would take an exceptionally long time and, thus, is not feasible within a normal laboratory time frame. However, in a first approximation, it is reasonable to assume that the same mechanism controls deformation in both temperature ranges since the average temperature in the lower range (≈ 900 °C) is only 150 °C lower than the lowest temperature in table 1.

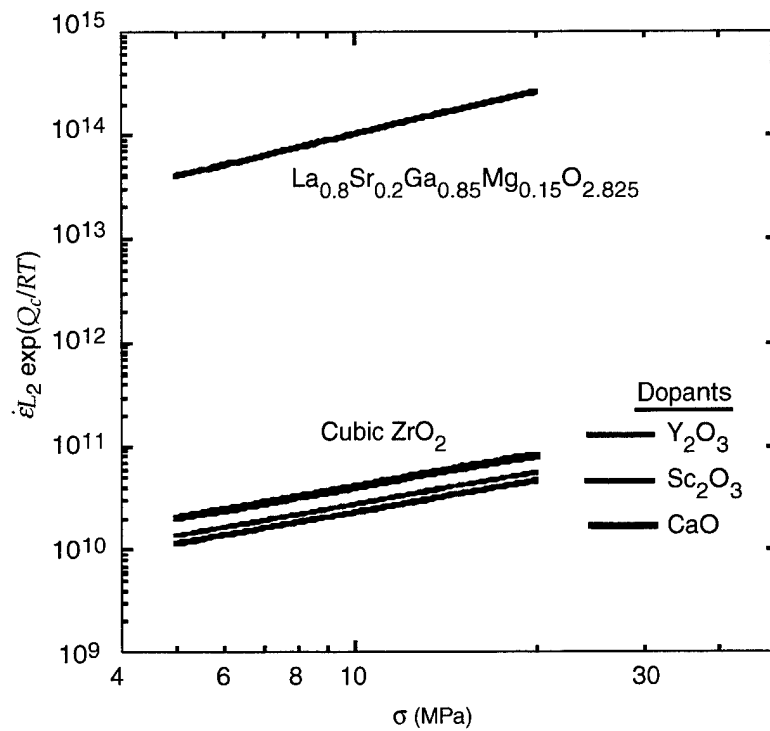
Using the above two assumptions and the data from table 1, the intrinsic creep resistance of cubic zirconia and LSGM-2015 are shown in figure 1. The data in figure 1 are plotted as grain size and temperature-compensated steady-state creep rate versus applied stress on a double logarithmic scale. From figure 1 several points are observed. First, the creep data after compensation for cubic zirconia from different sources with different dopants are in excellent agreement with each other. Second and most important, at a given value of applied stress, the temperature-compensated steady-state creep rate for LSGM-2015 is between 1,000 to 4,000 times faster than that for cubic zirconia. This result reveals that the intrinsic creep resistance of cubic zirconia is much higher than that for LSGM-2015. One possible explanation for this is the difference in crystal

structures: fluorite [19] for cubic zirconia versus monoclinic [20] or some other structure for LSGM-2015 (this might be orthorhombic [21] or cubic [1,22], as several different crystal structures have been suggested for single-phase LSGM-2015). More work is needed to understand this difference.

Table 1. Creep parameters for two materials.

| Material | Grain size (μm) | Temperature ($^{\circ}\text{C}$) | n | p | m | Q_c (kJ/mol) |
|---|------------------------------|------------------------------------|----------|----------|-----|----------------|
| $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ [5,14] | 8 | 1050–1300 | 1.3 | 1.8 | 0 | 521 |
| Cubic zirconia [9–13] | 1–20 | 1050–1600 | ~ 1 | ~ 2 | 0 | 460 |

Figure 1. Grain size and temperature-compensated steady-state creep rate versus applied stress for $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_{2.825}$ [5,14] and cubic zirconia [9,10]. The dopants for ZrO_2 are shown in the figure.



Conclusion

Knowledge of the creep parameters n , p , m , and Q_c for cubic zirconia and LSGM-2015 allowed for a determination of the intrinsic creep resistance of each material in the temperature range from 800 to 1000 °C, where they are to be utilized as electrolytes in solid oxygen fuel cells. The results reveal that the intrinsic creep resistance of the currently used cubic zirconia is much better than that for the recently discovered LSGM-2015 over the entire temperature range. This is most likely a result of the difference in their crystal structures.

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