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DIFFUSION-CONTROLLED CREEP IN MIXED-CONDUCTING OXIDES *

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Abstract

The steady-state creep rate of mixed-conducting oxides, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, for $x = 0.1, 0.15$, and 0.25 , and $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ has been investigated at temperatures between 1150 and 1300°C . Creep parameters and transmission electron microscopy observations indicate that deformation is controlled by lattice diffusion of one of the cations. The dependence of the creep rate on Sr concentration, combined with a point-defect model, confirms this hypothesis; however, the oxygen partial pressure dependence of creep (from 10^{-1} to 2×10^4 Pa) cannot be accounted for within the framework of a simple point-defect model.

Introduction

Perovskite-structured oxides have received considerable attention for use as air electrodes in high-temperature solid-oxide fuel cells. The $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ system has the advantages of high electronic and ionic conductivity, chemical stability at operating temperatures of $\approx 1000^\circ\text{C}$, and approximately the same coefficient of thermal expansion as the yttria-stabilized zirconia electrolyte. An understanding of deformation is important for possible fabrication by hot pressing or extrusion. Also, it has been recently noted that these materials exhibit potentially important magnetic properties [1].

In addition, if deformation is controlled by diffusion as is often observed, the results can provide a convenient method of obtaining cation diffusion data, which because of the low diffusivities, may be difficult and tedious to determine by tracer techniques. The correlation between steady-state creep results and diffusion measurements has been well-established in several simple and complex oxide systems, ranging from CoO and MnO [2] to the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_x$ [3]. In the latter case, the agreement between the diffusivity of yttrium calculated from steady-state strain rate measurements at nearly constant stress with no adjustable parameters and the diffusion coefficients determined from sectioning measurements of tracers were excellent [3,4].

Published preliminary work on deformation of $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ suggests that deformation is controlled by a diffusional creep mechanism with an activation energy of 490 kJ/mole, representing lattice diffusion of either La or Mn. The objective of this investigation was to extend the initial work to other compositions and oxygen partial pressures (P_{O_2}) to see whether this was a general conclusion for these perovskites and, if so, to relate the deformation results to diffusion and point-defect models.

Experimental Procedures

Processing of the mixed-conducting oxides has been described [5]. The powders were prepared by the glycine-nitrate process with high-purity nitrate precursors and glycine. The powders were precalcined in air at 650°C for 0.5 h to decompose any residual organic materials and then calcined at 1000°C for 1 h. Powders were uniaxially pressed into bars at 55 MPa, followed by isostatic pressing at 138 MPa. The bars were sintered in air at 1500°C for 4 h. Densities were between 89 and 93% of

theoretical. Samples approximately 2.0 x 2.0 x 4.0 mm were cut from the sintered bars with a low-speed diamond saw.

The microstructure of both the as-sintered and deformed samples was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). XRD analysis revealed that the as-sintered ceramic was single phase, with an orthorhombic perovskite structure. After thermal etching at 1200°C in air for 2 h, the grain size was determined by the linear intercept method. For the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ samples, the equiaxed grains were 5.2 ± 0.3 , 4.1 ± 0.3 , and 3.2 ± 0.4 μm for $x = 0.1$, 0.15, and 0.25, respectively. The grain size of the $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ material was somewhat larger, 7.5 ± 2.2 μm . These results are in accord with those of van Roosmalen et al. [6], who reported that the grain size of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ decreases with increasing Sr content. Samples for TEM were polished, dimpled, and then ion-milled to produce electron-transparent foils. In addition, the grain-shape form factor for a $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ specimen that was deformed 50% was measured before and after deformation.

Specimens were deformed in uniaxial compression under either a nearly constant strain rate [7], or under a nearly constant stress at the University of California, Irvine [8], or the University of Sevilla [9]. Experiments were performed in which strain rate or stress was varied at constant temperature and temperature or atmosphere was varied at constant stress. The test temperature ranged between 1150 and 1300°C, stresses from ≈ 3 to 30 MPa, and for the $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ specimens, the atmosphere was set at air, 1% O_2 , 1000 ppm O_2 , and Ar.

Results

Typical experimental results are shown in Fig. 1, in which the product of steady-state strain rate $\dot{\epsilon}$, and the grain size L^2 , are plotted as a function of stress σ . Generally, steady-state creep may be described by a phenomenological equation for the strain rate of the form, $\dot{\epsilon} = A \sigma^n L^p (\text{P}_{\text{O}_2})^m [\text{Sr}]^q \exp(-Q/RT)$, where A is a constant, $[\text{Sr}]$ is the Sr concentration x , Q is the activation energy, and RT has its usual meaning. The stress exponent n , and grain size dependence, p , are related to the deformation mechanism. On the other hand, m , q , and Q can be related to a point-defect model [2] because these terms are proportional to the diffusion coefficient of the rate-controlling species.

Figure 1. Plot of $\dot{\epsilon} L^2$ versus σ at 1250°C in air for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ for different x .

The slope of the lines in Fig. 1 is n and the values are given in Table 1. Stress exponents were also measured by load-change experiments. Within experimental uncertainty, the values for all compositions are equal to 1. As discussed in the paper on the deformation of $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ [5], the small grain size, the value of n close to unity, and the TEM observations that there is an absence of deformation-induced dislocations (Fig. 2) suggest that the deformation of these mixed-conducting oxides is controlled by a diffusional creep mechanism. Because of the fine grain size, lack of an

Table 1. Summary of deformation results.

Material	Atmosphere	n	Q (kJ/mole)	m @ 1230°C
La _{0.9} Sr _{0.1} MnO ₃	air	1.1 ± 0.2	490 ± 30	
La _{0.85} Sr _{0.15} MnO ₃	air	1.1 ± 0.2	475 ± 30	
La _{0.75} Sr _{0.25} MnO ₃	air	0.9 ± 0.2	460 ± 30	
La _{0.7} Ca _{0.3} MnO ₃	air	1.4 ± 0.5	380 ± 40	0.24*
La _{0.7} Ca _{0.3} MnO ₃	1% O ₂		405 ± 40	0
La _{0.7} Ca _{0.3} MnO ₃	1000 ppm O ₂		560 ± 60	0
La _{0.7} Ca _{0.3} MnO ₃	argon		360 ± 40	

*values of m were obtained for atmosphere changes from the row above to the row below the value in the table.

extensive transient creep regime, and the relatively high temperatures, it is assumed that a volume diffusion creep mechanism [10, 11] dominates. The results in Fig. 1 are, therefore, normalized by L^2 , although a fit to L^3 had about the same correlation factor as a fit to L^2 .

Figure 3 illustrates the determination of Q from a constant-stress experiment. The specimen was crept into a steady state at a constant stress of 10 MPa at 1150°C. The temperature was decreased by 20°C, and a new steady state $\dot{\epsilon}$ was measured. Q was calculated from the phenomenological creep equation given above. The values of Q for the various compositions are given in Table 1.

Figure 4 is an Arrhenius plot of the diffusivity of the La_{0.9}Sr_{0.1}MnO₃ creep data, calculated from the theoretical equation for Nabarro-Herring creep [10-12], $\dot{\epsilon} = BD_L\sigma\Omega/L^2kT$, where D_L is the lattice diffusivity of the rate-controlling species, B is a constant, chosen to equal 14 [11], and Ω is the molecular volume. The values of the oxygen diffusivity measured in La_{0.5}Sr_{0.5}MnO₃ [13], normalized by $2[V_{\dot{O}}] = [Sr']$ [5] (in Kröger-Vink notation) are also shown.

Optical photomicrographs of La_{0.7}Ca_{0.3}MnO₃ deformed 50% indicated that the grain shape was unchanged. The form factor was 0.9.

Figure 2. TEM photomicrograph of deformed La_{0.24}Sr_{0.76}MnO₃. Undeformed and deformed microstructures are identical; both show domains, partial dislocations, and some porosity.

Discussion

The following experimental evidence supports the conclusion that creep in these mixed-conducting perovskites is a diffusion-controlled process: 1. the stress exponent is equal to unity, 2. there are no dislocation networks in the deformed specimens, and 3. the activation energies for deformation are about equal for all of the investigated $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ materials. The fact that the form factor for the heavily deformed $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ remained unchanged implies that grain-boundary sliding, accommodated by diffusion, was the dominant mechanism rather than Nabarro-Herring creep, as was assumed in plotting Fig. 4. However, the two models yield similar diffusion coefficients.

Figure 3. Plot of $\dot{\epsilon}$ versus ϵ for $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ at $\sigma = 11.3$ MPa for P_{O_2} : I – 4.6×10^{-1} , II – 5×10^2 , III – 2.5×10^3 , and IV – 2×10^4 Pa.

Figure 4. Arrhenius plot of diffusivity calculated from creep experiments on $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$. The oxygen diffusivity normalized for $x = 0.1$ is also shown [5].

The Q for creep of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ in air appears to be somewhat lower than the Q reported for the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ system and it also appears that a rather abrupt change occurred in Q at 1000 ppm O_2 . These results, however, must be viewed as preliminary until further confirmation.

Few, if any, diffusion coefficients for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ have been measured. Oxygen diffusion has been measured for $x = 0.5$, but only over the temperature range of 700–900°C. We are unaware of existence any cation diffusion measurements in this system. A comparison of the extrapolated oxygen diffusion data with the creep data (Fig. 4) indicates that Q for the creep process is about a factor of

two higher than Q for oxygen diffusion. Oxygen diffusion has been measured up to 1000°C in single crystals of a similar system, $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$ [14], and Q was found to be 270 ± 38 kJ/mole, in fair agreement with the 232 ± 8 kJ/mole measured in the temperature range of 400 – 600°C for polycrystals [15]. Therefore, the Q measured for creep is likely to be too high to represent anion diffusion. On the other hand, values of Q for cation diffusion in similar systems are higher than those measured for anion diffusion [16] and lie much closer to the values measured for creep. Therefore, on the basis of the magnitudes of activation energies, it can be stated that it is likely that cation diffusion controls deformation.

We are unaware of a defect model for the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ system; hence, we will use a simple defect model developed by Flandermeyer et al. [17] to explain thermogravimetric measurements of the defect properties of Mg-doped LaCrO_3 , a system which should exhibit a similar behavior. Several assumptions are made: 1. p-type disorder prevails, 2. all defects are fully ionized, 3. vacancies rather than interstitials are the main defects, 4. cation stoichiometry must be maintained (concentration of La and Mn vacancies are equal), and 5. Sr^{+2} substitutes for a cation on a normal La site [17, 18]. The relevant equations are:

$$1. \text{ Schottky equilibrium: } \text{nil} \Leftrightarrow V_{\text{La}}''' + V_{\text{Mn}}''' + 3V_{\text{O}}', \quad (1)$$

$$2. \text{ Charge neutrality: } 2[V_{\text{O}}'] + p = 6[V_{\text{Mn}}'''] + [\text{Sr}'_{\text{La}}], \quad (2)$$

$$3. \text{ Oxygen incorporation: } \frac{3}{2}\text{O}_2 \Leftrightarrow V_{\text{La}}''' + V_{\text{Mn}}''' + 3\text{O}_\text{o}^\times + 6p. \quad (3)$$

Using assumption 4, $[V_{\text{Mn}}'''] = [V_{\text{La}}''']$, and assuming that both V_{O}' and V_{Mn}''' are small when compared with $[\text{Sr}'_{\text{La}}]$, it has been shown [16] that

$$[V_{\text{Mn}}'''] = K_1(P_{\text{O}_2})^{3/4}[\text{Sr}'_{\text{La}}]^{-3} \quad (4)$$

and

$$[V_{\text{O}}'] = K_2[\text{Sr}'_{\text{La}}]^2(P_{\text{O}_2})^{-1/2}. \quad (5)$$

Equations 4 and 5 predict the dependence of the cation and anion vacancy concentrations on both the amount of Sr and P_{O_2} . The diffusion coefficient is, of course, proportional to the concentration.

Figure 5. Variation of the normalized strain rate with concentration of Sr in the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ system.

Figure 5 presents the dependence of the normalized strain rate as a function of Sr concentration in the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ system. The slope of this data q , is equal to -1.4 ± 0.2 . Comparison of the data with Eqs. 1 and 2 indicates that if cations control creep, $\dot{\epsilon}$ should decrease with increasing $[\text{Sr}]$, but if anions control, $\dot{\epsilon}$ should increase. The fact that the $\dot{\epsilon}$ decreases with $[\text{Sr}]$ is further indication that a cation is the rate-controlling species. This conclusion is in accord with the observation that grain size decreases with increasing $[\text{Sr}]$ [5], which can be related to a decreased diffusivity as a result of adding $[\text{Sr}]$. In light of all of the simplifying assumptions in the defect model, it is probably not surprising that the exponent is different from the value of -3 predicted from Eq. 4.

However, Eq. 4 predicts that $\dot{\epsilon}$ should increase with increasing P_{O_2} . Such an increase has not been observed in the preliminary experiments with $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, despite the fact that the range of measured P_{O_2} should have produced a significant effect. The values of m in Table 1 are very close to 0. It is clear that experiments over a wide range of P_{O_2} in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ will be necessary to address this point.

Summary

Steady-state creep of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ at temperatures from 1150 to 1300°C is controlled by a diffusional process. Activation energies and diffusion coefficients have been extracted from the creep data. The activation energies and the dependence of the creep rate on Sr concentration indicate that one of the cations is the rate-controlling species. However, it is not possible to identify whether it is the A- or B-site cation. The predictions of a simple defect model are not in complete accord with the measurements, particularly for the oxygen partial pressure dependence of creep in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. Considerable additional experimental and theoretical work will be required.

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