USE OF CREEP TO INVESTIGATE MASS TRANSPORT IN (La,Sr)MnO₃

J. Wolfenstine
Army Research Laboratory
AMSRL-SE-DC
2800 Powder Mill Road
Adelphi, MD 20783-1197

R. E. Cook, K. C. Gorett and J. L. Routbort
Argonne National Laboratory
bMaterials Science Division
cEnergy Technology Division
Argonne, IL 60439-4838

ABSTRACT

The creep behavior of fine-grained (La₁₋ₓSrₓ)₁₋₂yMnO₃ (LSM) with x=0.1, 0.2 and 0.3 and y=0.03 to 0.04 was investigated as a function of oxygen partial pressure (PO₂) at 1250°C. For (La₁₋ₓSrₓ)₁₋₂yMnO₃ with x=0.1, 0.2 an oxygen partial pressure exponent, m=0.25 was observed at low oxygen partial pressures. At high oxygen partial pressures, m=-0.16. For (La₀.₇Sr₀.₃)₁₋₂yMnO₃ only, m=0.25 was exhibited over the entire PO₂ range tested. The m values were not in agreement with the simple point defect model for LSM. The simple defect-chemistry model for LSM was modified based on cation non-stoichiometry. The modified defect-chemistry model yielded excellent agreement between the predicted and experimental m values. The effect of oxygen activity on deformation suggested that the rate-controlling defects are cation vacancies at low oxygen partial pressures and oxygen vacancies at high oxygen partial pressures.

INTRODUCTION

At present (La,Sr)MnO₃ (LSM) is considered as one of the most promising cathode materials for use in high-temperature solid oxide fuel cells (SOFCs). However, at present no studies have been conducted to investigate the high-temperature mechanical properties of this material. Investigation of the high-temperature mechanical properties is important for the following reasons: 1) to ascertain dimensional stability at temperature under load, 2) to fabricate into complex shapes that may be required in certain applications and 3) to determine diffusion coefficients and construct defect-chemistry models. This information is important for processing because, both sintering
and grain growth are controlled by the same species that controls high-temperature deformation.

It was previously shown that the creep behavior of fine-grained (<10 μm) (La, Sr)MnO<sub>3</sub> in the temperature range 1100 to 1300°C deformed in air was controlled by grain boundary sliding accommodated by cation lattice diffusion via a vacancy mechanism (1,2). However, one important question remained unanswered. Does the rate-controlling species and defect (cation lattice diffusion via a vacancy mechanism) change with oxygen partial pressure since, the previous experiments were conducted at a single oxygen partial pressure. It is the purpose of this paper to answer this question.

**EXPERIMENTAL**

(La<sub>1-x</sub>Sr<sub>x</sub>)<sub>1-y</sub>MnO<sub>3</sub> samples with x=0.1, 0.2 and 0.3 and y=0.3 to 0.4 were used in this study. Powders were prepared by a glycine-nitrate combustion synthesis process. The powders were calcined and sintered. Rectangular parallelopipeds for creep testing with a ratio of height to width of approximately 2:1 with a typical sample being 3 mm x 3 mm x 6 mm were cut from the sintered bars. The rectangular parallelopipeds specimens were deformed in uniaxial compression under constant strain rates at different oxygen partial pressures (PO<sub>2</sub>). PO<sub>2</sub> change tests were conducted to determine the value of the oxygen partial pressure exponent, m. All tests were conducted at 1250°C. The testing temperature and the strain rates were based on previous work (1,2). The PO<sub>2</sub> ranged from 1 x 10<sup>-2</sup> to 1 x 10<sup>5</sup> Pa. Samples were typically held for times of 1 to 1.5 hours at a given PO<sub>2</sub> prior to the application of the imposed constant strain rate. Based on the sample dimensions and the chemical diffusivity of oxygen this time should be sufficient to insure that the sample was in equilibrium with the test atmosphere (3).

**RESULTS AND DISCUSSION**

X-ray diffraction revealed that all three materials were single phase with a relative density of about 90% and with equiaxed grains of grain size of 1 to 3 μm (3).

The dependence of the steady-state stress, σ, on PO<sub>2</sub> was determined using the following relation:

\[
\sigma = A \text{PO}_{2}^{m}
\]

where m is an exponent whose sign and magnitude provide an indication of the rate-controlling species and defect (4-6) and A is a constant for a fixed temperature, composition and microstructure. The dependence of σ on PO<sub>2</sub> for (La<sub>0.9</sub>Sr<sub>0.1</sub>)<sub>1-y</sub>MnO<sub>3</sub> and (La<sub>0.7</sub>Sr<sub>0.3</sub>)<sub>1-y</sub>MnO<sub>3</sub> are shown in Figs. 1 and 2, respectively. The data are plotted as strain rate and grain size compensated σ versus PO<sub>2</sub> on a double logarithmic scale. The stress has been normalized to account for variations in the stress due to differences in strain rates and grain sizes (3). The slope of the curves is -m. From Fig. 1 it can be seen at low PO<sub>2</sub> (<10 Pa) that m is positive (negative slope) whereas at high PO<sub>2</sub> (>100 Pa) m becomes negative (positive slope). Similar behavior was observed for the (La<sub>0.8</sub>Sr<sub>0.2</sub>)<sub>1-y</sub>MnO<sub>3</sub> material. From Fig. 2 for (La<sub>0.7</sub>Sr<sub>0.3</sub>)<sub>1-y</sub>MnO<sub>3</sub> only a positive m
(negative slope) was exhibited over the entire PO2 range tested. The m values as a function of PO2 for \((La_{0.9}Sr_{0.1})_{1-y}MnO_3\), \((La_{0.8}Sr_{0.2})_{1-y}MnO_3\) and \((La_{0.7}Sr_{0.3})_{1-y}MnO_3\) are listed in Table I.

| Material                     | PO2 Range (Pa) | m     |
|------------------------------|----------------|-------|
| \((La_{0.9}Sr_{0.1})_{1-y}MnO_3\) | 10^2 to 10^3   | 0.25  |
| \((La_{0.8}Sr_{0.2})_{1-y}MnO_3\) | 10^2 to 10^5   | -0.19 |
| \((La_{0.7}Sr_{0.3})_{1-y}MnO_3\) | 10^1 to 10^5   | 0.27  |

The experimental m values can be compared to theoretical predictions to determine the rate-controlling specie and defect. The simple defect-chemistry model for LSM assumes the following (2,3,7-12): 1) p-type disorder prevails, 2) all defects are ionized, 3) Schottky equilibrium is dominant, 4) cation stoichiometry is maintained, 5) Sr substitutes for La and 6) the charge neutrality at the PO2s used in this study is given as follows, expressed in Kroger-Vink notation:

\[ p = [Sr]^\delta \]  

Use of the above assumptions yields the following expressions for the cation and oxygen vacancy concentrations as a function of PO2:

\[ [V_{\text{Mn}}]^\gamma \propto PO_2^{3/4} \]  

\[ [V_{\text{O}}]^\gamma \propto PO_2^{-1/2} \]

Since the vacancy concentrations are inversely proportional to the steady-state stress, \( \sigma \), the simple defect model predicts, from Eqns. 3 and 4, \( m = 0.75 \) for cation vacancies and \( m = -0.50 \) for oxygen vacancies. If these values are compared to the experimental values listed in Table I for the LSM materials it is observed that the simple point-defect is not in agreement with the experimental values determined from creep.

A major assumption in the simple defect chemistry model is that cation stoichiometry is maintained. In other words, the concentration of A- and B-site cation vacancies are equal. It has been recently shown by neutron diffraction that this assumption may not be valid (13). Thus, the simple model must be modified to take into account this factor. Recently, Abrantes et al. (14) and Cook (3) have derived a new defect model for LSM that incorporates cation non-stoichiometry. For the case of A-site deficient LSM, the materials used in this study, the cation vacancy concentrations can be expressed as follows:

\[ [V_{\text{Mn}}]^\gamma = [V_{\text{Mn}}] + y \]

Equation 5 with assumptions 1, 2, 3 and 6 of the simple defect model yields the following expressions for the cation and oxygen vacancy concentrations as a function of PO2:

\[ [V_{\text{La}}]^\gamma \propto PO_2^{1/4} \]

\[ [V_{\text{O}}]^\gamma \propto PO_2^{-1/6} \]

From Eqns. 6 and 7, it can be seen that the modified defect model predicts \( m = 0.25 \) for cation vacancies and \( m = -0.16 \) for oxygen vacancies. These values are in excellent agreement with experimental values listed in Table I.
Thus, several important conclusions can be reached. Firstly, the modified defect-chemistry model is in better agreement with creep data than the simple defect chemistry model. Secondly, at low PO2s for (La0.9Sr0.1)1-yMnO3 and (La0.8Sr0.2)1-yMnO3 cation vacancies are the rate-controlling defects. Thirdly, at high PO2s for (La0.9Sr0.1)1-yMnO3 and (La0.8Sr0.2)1-yMnO3 oxygen vacancies are the rate-controlling defect. Fourthly, over the entire PO2 range tested for (La0.7Sr0.3)1-yMnO3 cation vacancies are the rate-controlling defect. Based on the data in Table I and Eqns. 6 and 7 a Brouwer diagram which shows the point-defect concentrations in LSM as a function of PO2 is shown in Fig. 3. From Fig. 3 it is observed that at low PO2s that cation vacancies should control creep whereas at high PO2s oxygen vacancies are the defect that control creep.

It is important to note that the previous creep results (1,2) suggested that the creep rate was controlled by cation vacancies at a PO2 according to Fig. 3 that should be in a region where oxygen vacancies are the rate-controlling defect. This apparent discrepancy can be rationalized using the modified-defect model. In the modified point defect model the crossover PO2 between cation and anion control is a function of cation non-stoichiometry. The model predicts that cation vacancy control will shift to a higher PO2 as the A-site deficiency decreases. The previous LSM materials were A-site excess with y=-0.025. Thus, cation vacancies should control creep in the previous materials to higher PO2s than in the present study. This is in agreement with the experimental results. Hence, the creep results for the materials used in this study and previously are in agreement with the modified point defect model.

SUMMARY

The creep behavior of fine-grained (La1-xSr)x1-yMnO3 (LSM) with x=0.1, 0.2 and 0.3 and y=0.03 to 0.04 was investigated as a function of oxygen partial pressure (PO2) at 1250°C. The m values were not in agreement with the simple defect chemistry model for LSM. The simple defect-chemistry model for LSM was modified based on cation non-stoichiometry. The modified defect-chemistry model yielded excellent agreement between the predicted and experimental m values. The effect of oxygen activity on deformation suggested that the rate-controlling defects are cation vacancies at low oxygen partial pressures and oxygen vacancies at high oxygen partial pressures.

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Fig. 1. Normalized stress versus PO2 for (La0.55Sr0.10MnO3+δ).

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Fig. 2. Normalized stress versus PO$_2$ for (La$_{0.7}$Sr$_{0.3}$)$_{y}$MnO$_3$.

Fig. 3. Point defect concentration for Sr doped LaMnO$_3$ as a function of the oxygen partial pressure.

\[ [V_{o^{2-}}] \approx 0.5[Sr_{La}] \]

\[ [V_{La^{+}}^\prime] \approx (PO_2)^{1/4} \]

\[ [V_{o^{2-}}] \approx (PO_2)^{-1/5} \]

\[ [V_{La^{+}}^\prime] \approx [Sr_{La}]^{-3/2} \]