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DEFORMATION OF NONSTOICHIOMETRIC CuO POLYCRYSTALS

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DEFORMATION OF NONSTOICHIOMETRIC CuO POLYCRYSTALS

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INTRODUCTION

The current interest in fabrication methods for high temperature superconductors has fostered heightened interest in the precursor materials. It has been shown that the reaction kinetics for formation of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$, $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ and $\text{YBa}_2\text{Cu}_3\text{O}_x$ are related to the copper oxide precursor through both the size of the starting powder¹ and the oxidation state,^{2,3} with finer CuO powders reacting faster. Many proposed fabrication methods include a high temperature mechanical working step during the reaction process.^{4,5} However, little is known about the diffusional and mechanical properties of CuO at the fabrication temperatures of interest. The literature indicates only that the electrical conductivity of CuO is independent of the oxygen partial pressure (P_{O_2}).^{6,7} Therefore, only intrinsic ionization occurs for CuO. Thus, for a given temperature, the concentrations of electrons and holes are fixed.

In this study, compression creep was employed to shed light upon the diffusion of rate-controlling defects in nonstoichiometric CuO. Tests were performed on polycrystalline samples over a range of temperature (T), P_{O_2} , and strain rate ($\dot{\epsilon}$). Data were analyzed with standard equations for steady-state creep.⁸ Electron microscopy was used in conjunction with the data analysis to identify the operative creep mechanisms. These results for CuO will be contrasted with previous work performed on another copper oxide compound, Cu_2O .⁹

EXPERIMENTAL PROCEDURES

Compression creep samples were fabricated from CuO powder. The starting powder was formed by decomposing $\text{Cu}_2\text{CO}_3(\text{OH})_2$ in flowing O_2 at 750°C for 24 h, which is one method used to produce CuO superconductor precursor. X-ray diffraction detected only CuO after the heat treatment. Bars were isostatically pressed at a pressure of 70 MPa from a mixture of 5 wt. % polyethylene glycol and 95 wt. % CuO powder. The bars were sintered in shallow Al_2O_3 crucibles in flowing O_2 at 995°C for 12 h. The finished bars had a density of 5.5 g/cm^3 which is 86% of the theoretical density.⁶ Square column samples ($\approx 2 \times 2 \times 4$

mm) were sliced from the sintered bars. The average linear intercept grain size was determined to be $\approx 35 \mu\text{m}$ from scanning electron microscopy (SEM) of polished surfaces.

An Instron machine fitted with a high-temperature furnace modified for atmosphere control was used for the compression tests. Testing procedures have been described in depth previously.¹⁰ Tests were conducted from 884°C to 992°C, in a strain rate range from 2.5×10^{-6} to $2 \times 10^{-5} \text{ s}^{-1}$, in three different atmospheres: 100% oxygen, air and a mixture of 8% O_2 / 92% Ar. Sample fracture occurred at lower temperatures and at higher strain rates. Higher temperatures were not used in an attempt to avoid grain growth and Cu volatilization. Lower strain rates were not used because they could not be reliably maintained with the equipment. Load (L) vs. time (t) data were collected with the aid of a computer. Stress (σ) vs. strain (ϵ) was calculated from the load vs. time data under the assumption of uniform deformation. This assumption was verified by measurements of the dimensions of the samples before and after testing. No barreling of the samples was detected and total strains were limited to less than $\approx 10\%$. The strain rates were referenced to the initial sample length. Both transmission electron microscopy (TEM) and SEM were used to examine the post-test samples. The geometric density was measured both before and after the testing.

RESULTS

A typical σ as a function of ϵ analysis is shown in Figure 1. Steady state σ was realized within 1% of ϵ for most $\dot{\epsilon}$. At the faster $\dot{\epsilon}$, a decreasing maximum σ was observed with increasing ϵ . Tests were only considered to reflect steady-state in which the maximum σ decreased by less than 1%. Tests with a decrease greater than 1% were not used.

A plot of stress as a function of steady-state strain rate in oxygen for a variety of T is shown in Figure 2. The inverse slope of the line at each temperature is equal to the stress exponent (n) in the phenomenological creep equation,⁸

Figure 1: Stress as a function of strain measured at various strain rates in Oxygen at 975°C.

Figure 2: Stress as a function of strain rate for various testing temperatures.

$$\dot{\epsilon} = A \sigma^n \text{PO}_2^m \exp \left(\frac{Q}{RT} \right) \quad (1)$$

where A is a constant, m is the PO_2 exponent, Q is the activation energy for creep, and R is the gas constant. The value of $n = 2.96 \pm 0.45$ is based on data from 32 tests.

A plot of the log of σ as a function of the log of the PO_2 is shown in Figure 3 for two $\dot{\epsilon}$. The slope of the line at each $\dot{\epsilon}$ is equal to m . The value of m was determined to be 0.43 ± 0.15 .

The activation energy, Q , was determined to be 362 ± 130 kJ/mol from,

$$Q = n R \left(\frac{\partial \ln \sigma}{\partial (1/T)} \right)_{\dot{\epsilon}, \text{PO}_2} \quad (2)$$

where the standard deviation of Q reflects the standard deviation of the least squares line and the standard deviation of n .

SEM analysis determined that negligible grain growth occurred during the creep testing. Additionally, no measurable densification was observed. Small cavities were frequently found at the grain boundaries. Cavitation was limited for the samples that experienced the lower $\dot{\epsilon}$ and higher test temperatures. However, the data were not included in the analysis of n and Q for the tests conducted at $\dot{\epsilon} = 2 \times 10^{-5} \text{ s}^{-1}$ and at lower temperatures and $\dot{\epsilon} = 1 \times 10^{-5} \text{ s}^{-1}$. An SEM micrograph showing typical cavities found at the higher $\dot{\epsilon}$ and lower T is shown in Figure 4. TEM investigations showed that the deformed samples appeared to have significantly higher dislocation density than the undeformed samples. Twinning was also seen in both the deformed and the undeformed samples. A typical dislocation microstructure is shown in Figure 5.

Figure 3: Stress as a function of Oxygen partial pressure for two different strain rates.

Figure 4: SEM micrograph of a semi-polished fracture surface of deformed CuO displaying cavitation.

Figure 5: TEM micrograph of deformed CuO displaying dislocation structures.

DICUSSION

The results determined above can only be considered valid if true steady states were achieved during the tests. One measure of steady state is reproducibility of σ . Most samples were used to determine more than one steady-state σ . After a presumable steady-state σ was achieved, the $\dot{\epsilon}$ was usually doubled and the σ was allowed to readjust. Returning to the initial $\dot{\epsilon}$, in most cases, resulted in returning to the initial σ within a few percent. The electron microscopy analysis should also be compatible with steady-state mechanisms. The presence of dislocation sub-structures (Figure 5) is consistent with steady-state creep mechanisms. In addition, it is difficult to separate creep strain from strain caused by either densification or cavitation. There was no change in the density of the samples and cavitation was limited, so virtually all of the strain can be attributed to creep strain. Therefore, true steady-state data were acquired and the results from analysis with Equation 1 are valid.⁸

A stress exponent $n \approx 3$ implies the operation of a dislocation creep mechanism. The activation energy, $Q \approx 360$ kJ/mol, is comparable to other first-row, transition-metal oxides that experience recovery creep (Table 1).^{9,11-20} The P_{O_2} dependence of creep can be predicted from defect chemistry if the process is diffusion controlled, which would be operative if the rate-controlling mechanism is dislocation climb. It is not known what the dominant defect is in CuO.^{7,19} However, for CoO, FeO, MnO and NiO, the cation defects dominate and the minority defects, of either oxygen vacancies or interstitials, control the creep rates.^{11,12,14,19,21-23} It can be presumed by analogy that oxygen defects move more slowly than cation defects in CuO and, therefore, control creep; oxygen ions are larger than copper ions.¹⁵

Table 1. Activation energies for dislocation recovery in some oxides.

Material	T _m (°K)	Q (kJ/mol)	$\frac{Q}{RT_m}$
CoO	2068	480 ^{11,12}	27.9
MgO	3125	640-750 ¹³	24.6-28.9
NiO	2257	540 ¹⁴	28.7
MnO	1973	405 ¹⁵	24.7
FeO	1642	290 ¹⁶	21.2
Fe ₂ O ₃	1838	340 ¹⁷	22.3
Al ₂ O ₃	2345	500 ¹⁷	25.7
Li ₂ O	>1973	336 ¹⁸	20.5
UO ₂	3151	500 ¹⁷	19.1
Y ₂ O ₃	2683	400 ¹⁷	17.9
CuO	1599	362	27.2
Cu ₂ O	1508	183 ⁹	14.4

The oxidation of CuO can be written in Kröger-Vink notation as either

Both interstitial and vacancy defects can have either a neutral, single or double charge with respect to the lattice. As an example, an oxygen vacancy can be doubly ionized

or an oxygen interstitial can be singly ionized

Six defect equilibrium equations can be written for the point defects, according to the laws of mass action and charge neutrality, as^{19,21,22}

$$K = \frac{1}{P_{O_2}^{1/2}[V_O]} \quad \text{or} \quad K_0 = \frac{[O_i]}{P_{O_2}^{1/2}} \quad (6)$$

$$K' = \frac{[h^{\bullet}]}{P_{O_2}^{1/2}[V_O^{\bullet}]} \quad \text{or} \quad K_1 = \frac{[O_i^{\bullet}][h^{\bullet}]}{P_{O_2}^{1/2}} \quad (7)$$

$$K'' = \frac{[h^*]^2}{P_{O_2}^{1/2}[V_{O^{**}}]} \quad \text{or} \quad K_2 = \frac{[O_i^*][h^*]^2}{P_{O_2}^{1/2}}. \quad (8)$$

It is known that for a given temperature, the concentrations of electrons $[e^-]$ and holes $[h^*]$ are independent of the partial pressure of oxygen and are fixed.⁷ It can be seen then that the concentrations of oxygen vacancies are proportional to P_{O_2} to the $-1/2$ power and that the concentrations of oxygen interstitials are proportional to P_{O_2} to the $1/2$ power, regardless of the charge state for any of the defects.

If diffusion of the oxygen defects dictates the climb-rate of dislocations, which in turn is the rate-controlling mechanism of deformation, then the dependence of the creep process on P_{O_2} can now be predicted. Creep rates will escalate as diffusion accelerates, and diffusion increases if the concentration of the dominant point defect increases. The creep rate is directly proportional to the product of steady-state σ and the diffusivity. The steady-state σ would decrease with increasing P_{O_2} if oxygen interstitials controlled the creep rate, and would be proportional to $P_{O_2}^{-1/2}$. The steady-state σ would be proportional to $P_{O_2}^{1/2}$ if oxygen vacancies controlled the creep rate. Within experimental error as shown in Figure 3, the steady-state σ for creep of CuO is proportional to $P_{O_2}^{1/2}$. Thus, oxygen vacancies are most likely to be the rate-controlling species.

The conjecture that oxygen defects are the minority defect present in CuO may not be valid. Frenkel and Schottky equilibria link copper interstitials and oxygen vacancies and, as such, creep rates might be dictated by copper interstitials. In this case the P_{O_2} dependencies just delineated would be the same. However, the relative sizes of the copper and oxygen ions as noted, and creep data from similar monoxides support the choice of oxygen vacancies as the rate-controlling defect.

Bretheau et al. performed steady-state compressive creep tests on polycrystalline Cu_2O . They found that for steady-state creep: stress exponent, $n = 5.4 \pm 0.4$; the P_{O_2} exponent, $m = 0.37 \pm 0.09$; and the activation energy $Q = 1.9 \pm 0.3$ eV (183 ± 29 kJ/mol).⁹ In addition, the dominant mechanism was determined to be recovery controlled creep by dislocation climb with the rate being controlled by oxygen diffusion.⁹ A comparison of the parameters determined for CuO and Cu_2O for steady-state creep are shown in Table 2. Both compounds

Table 2. Parameters for steady-state creep of polycrystalline samples.

	CuO	Cu_2O
Crystal Structure	Monoclinic	Cubic
n	2.96 ± 0.45	$5.4 \pm 0.4^*$
m	0.43 ± 15	$0.37 \pm 0.09^*$
Q	362 ± 130 kJ/mol	183 ± 29 kJ/mol*
Q/Tm	0.225 kJ/mol•K	0.121 kJ/mol•K
Mechanism	Recovery creep by dislocation climb - oxygen controlled.	Recovery creep by dislocation climb - oxygen controlled.*

* As reported by Bretheau et al.⁹

have a high stress exponent, an equivalent PO_2 exponent dependency, and the same creep mechanism. However, despite these similarities, Q/RT_m for Cu_2O is about half that for CuO . A comparison of the activation energies for creep in the dislocation recovery regimes for other materials indicates that, despite the diversity of crystal structures and melting points, the Q/RT_m are all of the order of the value for CuO and that only Cu_2O falls significantly outside the vicinity.

CONCLUSIONS

Polycrystalline CuO , 86% dense, was crept in steady-state over the temperature range of 884 to 992°C. The creep rate of polycrystalline CuO can be expressed as

$$\dot{\epsilon} = A \sigma^{2.96 \pm 0.45} P_{O_2}^{0.43 \pm 0.15} \exp \left(\frac{-362 \pm 130 \text{ kJ/mole}}{RT} \right) \quad (9)$$

The data, supported by TEM observations, indicated that the kinetics of creep were controlled by dislocation motion by climb. The diffusion was controlled by motion of either oxygen vacancies or copper interstitials as evidenced by the PO_2 dependency, similar to Cu_2O . It is considered that oxygen vacancies are the more reasonable controlling defect. The presence of limited grain boundary cavitation was significant only for the high-strain-rate tests.

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