Electronic Transport Properties in Copper Oxides

by J.-H. Park and K. Natesan

Argonne National Laboratory, Argonne, Illinois 60439
operated by The University of Chicago
for the United States Department of Energy under Contract W-31-109-Eng-38
Argonne National Laboratory, with facilities in the states of Illinois and Idaho, is owned by the United States government, and operated by The University of Chicago under the provisions of a contract with the Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Reproduced from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831
Prices available from (615) 576-8401, FTS 626-8401

Available to the public from the National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
ELECTRONIC TRANSPORT PROPERTIES IN COPPER OXIDES

by

J.-H. Park and K. Natesan

Materials and Components Technology Division

July 1991

Work sponsored by

U. S. DEPARTMENT OF ENERGY
CONTENTS

ABSTRACT ............................................................................................................... 1

1  INTRODUCTION ......................................................................................... 1
   1.1 Defects and Transport in Copper Oxides ........................................... 1
   1.2 Oxidation of Copper ........................................................................... 3

2  EXPERIMENTAL PROCEDURE ................................................................. 5
   2.1 Sample Preparation .......................................................................... 5
   2.2 Oxidation Tests ............................................................................... 5
   2.3 Electrical Conductivity Measurements ............................................. 5
   2.4 Thermodynamic Measurements ....................................................... 6

3  RESULTS AND DISCUSSION ................................................................. 6
   3.1 Oxidation of Copper ......................................................................... 6
   3.2 Electronic States in Copper Oxide Systems ......................................... 12
   3.3 Electrical Conductivity .................................................................... 12
   3.4 Defect Species in Electronic Transport .............................................. 16
   3.5 Thermodynamic Considerations ....................................................... 19
   3.6 Hole Mobility .................................................................................... 25

4  SUMMARY .................................................................................................. 30

ACKNOWLEDGMENTS ..................................................................................... 32

REFERENCES ................................................................................................... 32
<table>
<thead>
<tr>
<th>FIGURES</th>
<th>PAGES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Schematic of electrical conductivity and weight change apparatus</td>
<td>6</td>
</tr>
<tr>
<td>2 Typical plot of weight gain vs. oxidation time</td>
<td>7</td>
</tr>
<tr>
<td>3 Typical plot for determining parabolic rate constant, kp, at initial stage of oxidation</td>
<td>7</td>
</tr>
<tr>
<td>4 Log kp vs. 1/T for oxidation of copper in oxygen</td>
<td>8</td>
</tr>
<tr>
<td>5 Fracture surfaces and oxide morphology at several temperatures between 350 and 900°C</td>
<td>9</td>
</tr>
<tr>
<td>6 Weight gain vs. time curves at 1000°C</td>
<td>10</td>
</tr>
<tr>
<td>7 Thickness of CuO phase vs. 1/2-power of time at 1000°C in oxygen</td>
<td>11</td>
</tr>
<tr>
<td>8 X-ray diffraction pattern for whiskers formed during oxidation of copper</td>
<td>11</td>
</tr>
<tr>
<td>9 EDS spectrum for Cu2O</td>
<td>12</td>
</tr>
<tr>
<td>10 Intensity ratio for Cu(I) to Cu(Kα) transition for various copper valences</td>
<td>13</td>
</tr>
<tr>
<td>11 Log conductivity vs. log pO2 at several temperatures, and expanded plot near Cu2O/CuO phase transition</td>
<td>14</td>
</tr>
<tr>
<td>12 Log conductivity vs. 1/T for nonstoichiometric Cu2O at pO2 = 10^-4 atm</td>
<td>15</td>
</tr>
<tr>
<td>13 Log conductivity vs. 1/T for CuO</td>
<td>15</td>
</tr>
<tr>
<td>14 Log pO2 vs. 1/T for Cu/Cu2O and Cu2O/CuO phase boundaries</td>
<td>17</td>
</tr>
<tr>
<td>15 Conductivity vs. pO2^1/n for n = 1 to 8</td>
<td>19</td>
</tr>
<tr>
<td>16 Electrical conductivity vs. pO2^1/6 at temperatures between 700 and 1100°C</td>
<td>20</td>
</tr>
<tr>
<td>17 Log σ_{int} vs. 1/T for calculated thermal gap based on slope of 1.2 eV for Cu2O</td>
<td>20</td>
</tr>
<tr>
<td>18 Optical gap energy vs. temperature for Cu2O</td>
<td>21</td>
</tr>
<tr>
<td>19 Hole mobility vs. 1/T in nonstoichiometric Cu2O</td>
<td>22</td>
</tr>
</tbody>
</table>
20 Body-centered-cubic cell of Cu₂O ................................................... 23
21 Log σnoon vs. log pO₂ ......................................................................... 23
22 Log slope (dσ/dpO₂¹/₆) vs. 1/T for Cu₂O ........................................ 24
23 pO₂¹/n vs. change of stoichiometry for two examples; log x vs. pO₂¹/₆
    fit for data in Ref. 6; and replot of (b) as log x vs. log pO₂ ............... 26
24 Simultaneous measurements of electrical conductivity and weight
    change in inert environment of argon gas ........................................ 27
25 Typical plots for results of simultaneous measurements of electrical
    conductivity and pO₂ for constant composition measurement and
    collected data plot for log conductivity and log pO₂ vs. 1/T ................. 28
26 Calculated oxygen formation enthalpy, ΔHO₂, and hole conduction
    energy, E₇ ..................................................................................... 29
27 Electrical conductivity change with pO₂ associated with
    decomposition of Cu₂O → Cu + CuO ............................................. 30
28 Cu₂O/CuO phase transition in terms of variation of EMF vs.
    temperature, variation of oxygen concentration in gas phase, and
    electrical conductivity variation during transition ............................ 31

TABLES

1 Possible defects in nonstoichiometric Cu₂O ....................................... 2
2 Physical parameters of Cu₂O and CuO .............................................. 4
3 Electron occupancy for different Cu valences .................................. 13
4 Calculated hole mobilities for Cu₂O ................................................. 21
ELECTRONIC TRANSPORT PROPERTIES IN COPPER OXIDES

by

J.-H. Park and K. Natesan

ABSTRACT

Oxidation of copper and electronic transport in thermally grown large-grain polycrystals of nonstoichiometric copper oxides were studied at elevated temperatures. Thermogravimetric copper oxidation was studied in air and oxygen at temperatures between 350 and 1000°C. From the temperature-dependence of oxidation rates, three different processes can be identified for the oxidation of copper: bulk diffusion, grain-boundary diffusion, and surface control with whisker growth; these occur at high, intermediate, and low temperatures, respectively. Electrical conductivity measurements as a function of temperature (350-1134°C) and \( p_{O_2} \) \((10^{-8}-1.0 \text{ atm})\) indicate intrinsic electronic conduction in CuO over the entire range of conditions. Electrical behavior of nonstoichiometric CuO indicates that the charge defects are doubly ionized oxygen interstitials and holes. The calculated enthalpy of formation of oxygen (\( \Delta H_{O_2} \)) and the hole conduction energy (\( E_H \)) at constant composition for nonstoichiometric Cu2O are 2.0 ± 0.2 eV and 0.82 ± 0.02 eV, respectively.

1 INTRODUCTION

1.1 Defects and Transport in Copper Oxides

Two copper oxides, i.e., Cu2O and CuO, are stable in the copper-oxygen system. Cuprous oxide, Cu2O, is known to be a metal-deficient, p-type semiconductor with cation vacancies and electron holes as the primary defects.\(^1\) The deviation from stoichiometry has been studied as a function of temperature and oxygen partial pressure by chemical analysis of quenched samples,\(^2\) by thermogravimetry,\(^3-5\) and by high-temperature solid-state coulometric titration.\(^6\) The data are inconsistent. These studies generally conclude that Cu2O is metal-deficient and that the prevailing atomic defects are neutral copper vacancies. However, several different models were proposed for the defect structure of nonstoichiometric Cu2O on the basis of previous studies. These include neutral\(^3-5\) (depicted in Eqs. 1 and 4 of Table 1), singly ionized copper vacancies\(^2,7\) (Eq. 5), singly ionized oxygen interstitials\(^8\) (Eq. 2), and doubly ionized oxygen interstitials (Eq. 3). The oxygen partial pressure (\( p_{O_2} \)) dependence of the electrical conductivity of Cu2O with various defects is also shown in the table.
Table 1. Possible defects in nonstoichiometric Cu$_2$O

<table>
<thead>
<tr>
<th>Point Defect</th>
<th>Charge</th>
<th>Expected Defect Reaction</th>
<th>Eq. No.</th>
<th>Exponent, $^a$ n</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_{i}^o$</td>
<td>0</td>
<td>$1/2 \text{O}<em>2 (g) = \text{O}</em>{i}^o$</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>O$_{i}^-$</td>
<td>-1</td>
<td>$1/2 \text{O}<em>2 (g) = \text{O}</em>{i}^- + h^-$</td>
<td>2</td>
<td>1/4</td>
</tr>
<tr>
<td>O$_{i}^{--}$</td>
<td>-2</td>
<td>$1/2 \text{O}<em>2 (g) = \text{O}</em>{i}^{--} + 2 h^-$</td>
<td>3</td>
<td>1/6</td>
</tr>
<tr>
<td>V$_{Cu}x$</td>
<td>0</td>
<td>$1/2 \text{O}<em>2 (g) = 2 \text{V}</em>{Cu}x + \text{O}_o x$</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>V$_{Cu}^-$</td>
<td>-1</td>
<td>$1/2 \text{O}<em>2 (g) = 2 \text{V}</em>{Cu}^- + \text{O}_o x + h^-$</td>
<td>5</td>
<td>1/8</td>
</tr>
<tr>
<td>V$_{Cu}^{--}$</td>
<td>-2</td>
<td>$1/2 \text{O}<em>2 (g) = \text{V}</em>{Cu}^{--} + \text{O}_o x + 2 h^-$</td>
<td>6</td>
<td>1/6</td>
</tr>
</tbody>
</table>

Intrinsic $e^-$ and $h^-$: $0 = e^- + h^-$

$^a$Exponents, $n$, in $\sigma \sim \text{pO}_2^{1/n}$ (pO$_2$ dependence of electrical conductivity).

The electrical conductivity ($\sigma$) of Cu$_2$O has been measured over a wide range of temperatures and pO$_2$ levels.$^7$, $^9$-$^{12}$ Maluenda et al.$^{14}$ measured electrical conductivity of Cu$_2$O over the temperature range 700-1100°C at a pO$_2$ corresponding to Cu$_2$O phase, down to $10^{-6}$ atm. According to their results, the slope (d$log \sigma$/d$log \text{pO}_2$) is greater than 1/8, which is not expected if V$_{Cu}^-$ is the only charged atomic defect. To account for the observed pO$_2$ dependence of $\sigma$, Maluenda et al.$^{14}$ suggest that a defect pair (V$_{Cu}^-$/V$_{Cu}x$) may become important with increasing pO$_2$. However, Peterson and Wiley$^{13}$ developed the exact expression for the electrical conductivity, which includes the coupling of singly ionized copper vacancies, V$_{Cu}^-$, and oxygen interstitials, O$_i^-$. They made two assumptions in analyzing their data: the mobility of the hole, $\mu_h^-$, was assumed to be independent of temperature, and the mobilities of V$_{Cu}^-$ and V$_{Cu}x$ were assumed to be equal. The enthalpy of formation values for the defects obtained from electrical conductivity measurements appears to be a function of both temperature and partial pressure,$^7$ and the values are not consistent with those deduced from thermogravimetric measurements.$^3$-$^5$

Because the deviation from stoichiometry in Cu$_2$O is rather small, quantitative agreement among the different studies is only fair. Peterson and Wiley$^{13}$ measured the temperature and pO$_2$ dependence of cation tracer diffusion in Cu$_2$O. The results suggested that both neutral and singly charged copper vacancies contribute mainly to cation self-diffusion. However, a defect model$^{13}$ involving both neutral and singly charged copper vacancies, holes, and singly
charged oxygen-interstitial ions was developed and compared with the tracer-diffusion data, the electrical conductivity data obtained by Maluenda et al.,\textsuperscript{14} and the stoichiometry data of O’Keefe and Moore.\textsuperscript{15} The model (see, for example, Eq. 5 in Table 1) suggests that the majority of the neutral species in Cu$_2$O are neutral copper vacancies and therefore may not provide a good explanation for electronic transport.

Measurements of the chemical-diffusion coefficient in Cu$_2$O by electrical conductivity were reported by Maluenda et al.\textsuperscript{14} These authors interpret diffusion in terms of neutral copper vacancies that are very mobile. Tracer diffusion of the stable isotope $^{18}$O has shown that interstitial oxygen ions are the predominant atomic defect in the oxygen sublattice.\textsuperscript{15} However, pO$_2$ dependence of stoichiometries and electrical conductivity of nonstoichiometric Cu$_2$O is not consistent unless one considers a partial ionization of an extremely minor portion of the cation vacancies. In the present study, temperature and pO$_2$ dependence of electrical conductivity have been reevaluated in terms of intrinsic and nonstoichiometric defects in Cu$_2$O. Thermodynamic measurements of Cu$_2$O were conducted to establish the defect structures of the nonstoichiometric Cu$_2$O.

Data on nonstoichiometry of CuO are not available. The conductivity of CuO is not dependent on oxygen activity at high temperature because of significant intrinsic electronic exitation. Intrinsic ionization predominates, i.e., \(0 = e^+ + h^-\), and if one neglects the temperature dependence of electronic charge carriers, the activation energy of 1.1 eV suggests a band-gap of 2.2 eV in the temperature range of 700-900°C; transport studies on CuO are incomplete. Physical constants for Cu$_2$O and CuO are given in Table 2.\textsuperscript{16}

### 1.2 Oxidation of Copper

Multiphase scales of Cu$_2$O and CuO form on Cu oxidized in oxygen or air at high temperatures, depending on the thermodynamic stability of the oxides.\textsuperscript{3,17,18} The parabolic rate constant, kp, for the oxidation of copper depends on pO$_2^{1/4}$ when only Cu$_2$O forms. Mass transport mainly involves neutral copper vacancies.\textsuperscript{19-22} This implies that the majority of the copper vacancies in the outer layer of the scale have zero effective charges. The formation of neutral copper vacancies, VCux, was considered in Eq. 3. When the scale consists of Cu$_2$O and CuO at the scale/gas interfaces, the parabolic rate constant is independent of pO$_2$. However, to verify this pO$_2$ dependence of oxidation, high-purity specimens (=99.9999% Cu) are needed because impurities can have a significant effect on defect concentration in nonstoichiometric Cu$_2$O. The existence of even a very thin
Table 2. Physical parameters of Cu₂O and CuO

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cu₂O</th>
<th>CuO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>143.08</td>
<td>79.54</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1235</td>
<td>1326</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Cubic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pn3m(224)</td>
<td>C2/c</td>
</tr>
<tr>
<td>Zₐ</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Lattice parameters (Å)</td>
<td>a₀ = 4.2696 ± 0.0010</td>
<td>a₀ = 4.684 ± 0.005</td>
</tr>
<tr>
<td></td>
<td>b₀ = 3.425 ± 0.005</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c₀ = 5.129 ± 0.005</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(β₀ = 99.47 ± 0.17°)</td>
<td></td>
</tr>
<tr>
<td>Cell volume (10⁻²⁴ cm³)</td>
<td>77.833 ± 0.055</td>
<td>81.16 ± 0.17</td>
</tr>
<tr>
<td>Molar volume (cm³)</td>
<td>23.437 ± 0.016</td>
<td>12.02 ± 0.03</td>
</tr>
<tr>
<td>X-ray density (g/cm³)</td>
<td>6.1047 ± 0.0043</td>
<td>6.509 ± 0.014</td>
</tr>
</tbody>
</table>

ₐZ = number of gram formula weight per unit cell.

Source: Ref. 16.

Layer of a compound of a higher metal oxidation state on the scale surface can alter the dependence of the reaction rate on oxidant pressure. Recently, Onay and Rapp²³ performed in-situ oxidation of copper at 10⁻⁴ atm and 300°C. Their results indicate that the multiphase, multilayer scales form by dissociation of the Cu₂O scale, which loses contact with the copper substrate upon thickening and also leads to microchannels and oxygen-rich CuO formation in Cu₂O scales. Kaufman and Hawkins²⁴ performed optical luminescence measurements on thin films of Cu₂O on copper. They suggest that the rate of copper oxidation is limited by the diffusion of copper vacancies.

Mechanisms whereby CuO whiskers form during oxidation of copper may involve chemical vapor transport or condensation-evaporation, as well as short-circuit diffusion up the center of the whisker.²⁵ Rapp and Raynaud²⁶ have proposed that the growth mechanisms of pyramid and pits are related to those of whiskers.
2 EXPERIMENTAL PROCEDURE

2.1 Sample Preparation

Copper foil samples (99.999% Cu) were used for the oxidation tests. Thin copper foil (2.0 x 10.0 x 0.10 or 0.01 mm) was used to grow copper oxide samples for electrical conductivity measurements, and large-grain polycrystals of Cu$_2$O (99.999%) with a rectangular shape (3.0 x 7.5 x 1.53 mm) were used in four-probe electrical conductivity measurements, similar to our previous work. Platinum wires were used as electrical leads.

2.2 Oxidation Tests

Oxidation tests were performed in oxygen or in air with an electrobalance (CAHN Instruments, Inc.). Samples (thickness of 0.01-0.1 mm) were suspended with a platinum wire, and the reaction gases flushed the system at room temperature. The samples were heated in the reaction gas to the desired test temperature, and weight change was monitored with time. All samples were completely oxidized.

The samples were examined by scanning electron microscopy (SEM) and electron-energy-dispersive spectroscopy (EDS); X-ray diffraction (XRD) was also conducted. Because the platinum wires become brittle after cooling, EDS was conducted by focusing on the solid-state reaction between the copper oxides and the wire. According to this observation, copper ions migrated into the platinum wire at high temperatures.

2.3 Electrical Conductivity Measurements

A copper foil sample was introduced into the conductivity-measuring apparatus (Fig. 1), which was similar to the cell used by Maluenda et al. and used an yttria-stabilized-zirconia (YSZ) oxygen probe to monitor the EMF. Only the end of the cell consists of the YSZ disc with a pyrex glass seal. Air and several Ar/O$_2$ gas mixtures were used for the outside reference gas, and various pO$_2$ values were monitored with the YSZ oxygen sensor. Samples were oxidized in the furnace, and electrical conductivity was measured as a function of temperature and pO$_2$. Initially, conductivity was determined as a function of pO$_2$ at constant temperature by the standard-four probe method at a fixed DC current of 1 mA. The iR drop potential across the potential probe was monitored with a strip-chart recorder. Sensitivity of the measurements was adequate. No appreciable differences were observed because of polarization in the DC measurement at the temperatures of the present study. However, in the low-pO$_2$ region, it was difficult to obtain a stable pO$_2$; consequently, measurements were performed in flowing premixed Ar/O$_2$ gas mixtures.
Conductivity was also measured by switching from inert gases (e.g., argon or helium) to fixed sample compositions or by using the gas-tight sealing cell described in our previous publications. Some simultaneous measurements of electrical conductivity and weight change were also made in the experimental apparatus.

2.4 Thermodynamic Measurements

Thermodynamic measurements were performed, along with conductivity measurements, on large-grain Cu$_2$O polycrystals in the gas-tight electrochemical cell described in Refs. 27-29.

3 RESULTS AND DISCUSSION

3.1 Oxidation of Copper

Figure 2 shows a typical weight-gain-versus-time curve for the oxidation of pure Cu in flowing oxygen at temperatures between 350 and 1000°C. Parabolic rate constants, $k_p$, were obtained from the initial oxidation period, which normally gives a straight line in a plot of $(\text{weight})^2$ versus time (Fig. 3). Temperature-dependent oxidation rates in pure oxygen are plotted in Fig. 4. Three different oxidation mechanisms can be inferred from the microstructures and fracture surfaces of the thermally grown scales (Fig. 5) and from the
temperature dependence of the oxidation rates. At high temperatures, the oxide grain size was large and the calculated activation energy from the slope of log $k_p$-versus-inverse-temperature plot was 1.79 eV. From this information, we infer that the kinetics involve mainly bulk diffusion at high temperatures. At intermediate temperatures, grain-boundary transport or a short-circuiting process leads...
to an activation energy of 0.87 eV, and some small whiskers form on the oxide surface. At low temperatures, whisker formation on the surface is the rate-limiting process, with a high activation energy of 2.32 eV.

Some features of the bulk process were investigated by the moving Cu$_2$O/CuO phase boundary during oxidation. Figure 6 shows weight gain versus time during oxidation at 1000°C in oxygen, corresponding to the formation of the Cu$_2$O and CuO phases. The plateau in Fig. 6(a) corresponds to the conversion of Cu to Cu$_2$O phase by weight. In Fig. 6(b), total weight gain associated with the oxidation of Cu$_2$O to CuO accumulates over a longer time. Figure 7 represents the moving phase boundary of Cu$_2$O/CuO as Cu$_2$O is converted to CuO. The moving-boundary constant, $K_b$, at 1000°C was $7.45 \times 10^{-13}$ cm$^2$/s, which may be related to oxygen diffusion in the CuO phase. No literature information is available on atomic diffusion, but the trend can be expected from the structure of both phases: Cu$_2$O has an open structure, but CuO does not have available sites for fast atomic transport (Table 2).

Multiphase scales formed when Cu is oxidized in oxygen or air at high temperatures (such as Cu$_2$O and CuO) depend on thermodynamic stability of the oxides. Because such a scale is single-phase, irrespective of the oxidant pressure, the oxidation rate is determined only by the growth rate of the inner layer, as shown in Fig. 6. When the reaction proceeds at a $p_{O_2}$ below the dissociation pressure of CuO, a single-phase scale of pure Cu$_2$O forms. In this case, there is an increase in the concentration gradient of lattice defects in the scale, as well as in the rate of scale growth, with the increase of $p_{O_2}$. However, at higher $p_{O_2}$
levels (greater than the dissociation pressure of CuO), a thin layer of CuO forms on the scale surface. The concentration gradient of lattice defects in the Cu$_2$O layer, however, no longer depends on external oxygen pressure$^{19-22}$ because the concentration of defects at the Cu$_2$O/CuO phase boundary is now determined by the dissociation pressure of CuO, which at a particular temperature is constant.

Consequently, a further increase in oxygen pressure affects only the concentration gradient of lattice defects in the CuO layer, but does not, however, influence the overall rate of reaction because this rate depends only on the growth rate of the Cu$_2$O phase.

At temperatures $<750^\circ$C, whiskers grow on the oxide surface (Fig. 5). Chemical vapor transport, condensation/evaporation, and short-circuit diffusion up the center of the whisker have been suggested as mechanisms for whisker growth.$^{25}$ Rapp and Raymond$^{26}$ proposed that the growth for pyramids and pits are related to that of whiskers. The X-ray diffraction pattern for whiskers (Fig. 8) indicates that they are CuO. Oxides grown at temperatures $<750^\circ$C yielded a pure phase of Cu$_2$O that was verified by X-ray analysis.
Fig. 6. Weight gain vs. time curves at 1000°C: (a) initial stage of oxidation, in which the Cu$_2$O phase forms, and (b) complete oxidation of Cu$_2$O to CuO
Fig. 7. Thickness of CuO phase vs. 1/2-power of time at 1000°C in oxygen

Fig. 8. X-ray diffraction pattern for whiskers formed during oxidation of copper
3.2 Electronic States in Copper Oxide Systems

EDS analyses were performed on copper with different valences, i.e., Cu metal (zero), Cu$_2$O (+1), and CuO (+2). Figure 9 shows an EDS spectrum for Cu$_2$O with an electron beam current of 1 nA at 15 KeV. Figure 10 shows the intensity ratio of the Cu(I) to Cu(Kα) transition for the individual samples. To extend the profile for higher copper valences, sequential tests were conducted on YBa$_2$Cu$_3$O$_{6.98}$, which has an average copper valence of +2.3, and on KCuO$_2$ with a copper valence of +3. This sequence alters the number of electron occupancies in 3d orbital for different copper valences. The electronic transition probabilities and selection rules based on the wave mechanics; for the Cu(I) transition, the selection rules are Δl = +1 or -1, and Δn = 0, 1, 2, 3 · · ·; i.e., the Cu(I) transition is available electronic states from the 3d to 3p and 2p. The electron configuration for the Cu can be represented as shown in Table 3.

In Fig. 10, the intensity ratio, R = I$_{Cu(I)}/I_{Cu(Kα)}$, for the transition of Cu(I) to Cu(Kα) decreases as copper valence increases; the ratios for Cu metal and Cu$_2$O do not differ significantly. This indicates that the number of electrons in 3d are the same for both, as shown in Table 3. To obtain reliable data, consistent experimental conditions, such as the same working distance and angle of the electron beam in EDS measurements, are important.

3.3 Electrical Conductivity

Electrical conductivity was measured as a function of temperature and pO$_2$, and the data are shown in Figs. 11-13. Cu$_2$O/CuO transition is evident in Fig. 11(a). In Fig. 11(b), linear extrapolation of the conductivity of the Cu$_2$O phase to the CuO phase boundary yields a somewhat lower value than does the CuO conductivity, but this trend varies with temperature. Figure 12 shows the
activation energy for hole conduction (0.628 eV) at \( pO_2 = 10^{-4} \) atm. Previous investigators reported activation energies for electrical conductivity of 0.54 to 0.73 eV, depending on temperature and \( pO_2 \).

No \( pO_2 \) dependence was observed over the CuO phase stability region; this indicates that the intrinsic electronic defect is dominant. This trend extends to quite low temperatures (i.e., < 300°C), where impurities normally predominate. No evidence of contributions from additional defects was detected in the electrical
Fig. 11. (a) Log conductivity vs. log $pO_2$ at several temperatures, and (b) expanded plot near Cu$_2$O/CuO phase transition
Fig. 12. Log conductivity vs. $1/T$ for nonstoichiometric Cu$_2$O at $pO_2 = 10^{-4}$ atm

\begin{align*}
\text{"Cu}_2\text{O"} \\
\log pO_2 &= 10^{-4} \text{ (atm)} \\
E_a &= 0.628 \text{ eV}
\end{align*}

Fig. 13. Log conductivity vs. $1/T$ for CuO

\begin{align*}
\text{"CuO"} \\
E_a &= 1.01 \text{ eV}
\end{align*}
conductivity measurements. From the slope of the log $\sigma$ versus inverse temperature for CuO (Fig. 13), the thermal gap energy for intrinsic electronic semiconduction can be about 2.02 eV. This value agrees with literature values, namely, 1.95 to =2.0 eV.$^{31}$ Based on electrical conductivity measurements and literature data,$^{32}$ the phase transition boundary for Cu$_2$O/CuO in terms of pO$_2$ and inverse temperature is shown in Fig. 14.

### 3.4 Defect Species in Electronic Transport

The present analysis makes use of data from Maluenda et al.$^{14}$ and of data provided by C. L. Wiley.$^{†}$ Semiconducting oxides, e.g., copper oxides, can be characterized by a band structure$^{33}$ in which the conduction and valence bands are, respectively, primarily metal- and oxygen-like. For these materials, bulk transport is primarily by electronic carriers, and ionic conduction is generally negligible over most conditions of interest. In pure metal oxides, electronic carriers arise from intrinsic electronic disorder, and ionic defects are a consequence of stoichiometry associated with the solid-gas equilibrium, i.e., the oxidation/reduction process. For intrinsic disorder, as shown in Eq. 7 of Table 1, $0 \rightarrow e' + h'$, thermal hole generation across the band gap takes on the mass action form

$$np = N_C N_V \exp\left[-\frac{E_g}{kT}\right]$$

where $E_g$ is the band gap and $N_C$ and $N_V$ are the electron and hole effective density of states, respectively. Because each electron is compensated by a hole,

$$n_{\text{int}} = p_{\text{int}} = (N_C N_V)^{1/2} \exp\left(-\frac{E_g}{2kT}\right)$$

in which the subscript int denotes intrinsic carrier concentrations. The carrier concentration depends only on temperature. Therefore, total carrier concentration, $p$, can be represented by the sum of the carrier concentration from intrinsic defects (only the function of temperature) and from charge-compensating defects via the formation of nonstoichiometric (function of temperature and pO$_2$) reaction:

$$p = p_{\text{int}} + p_{\text{non}}$$

where $p_{\text{non}}$ represents the hole carriers deduced from nonstoichiometric defect reaction.

*Therefore, electronic transport in CuO depends largely on temperature, which suggests that this material can be used as a temperature sensor.

†Personal communication, 1990.
Therefore, total electrical conductivity is composed of the sum of the partial conductivities, $\sigma_j$, associated with each type of charge carrier, i.e.,

$$\sigma = \sum \sigma_j$$  \hspace{1cm} (11)

where $\sigma_j$ is defined by

$$\sigma_j = p_j z_j q \mu_j$$  \hspace{1cm} (12)

in which $p_j$ is the hole carrier concentration ($\text{cm}^{-3}$), $z_j q$ is the effective charge (in coulombs), and $\mu_j$ is the mobility ($\text{cm}^2/\text{V-s}$) of the $j_{th}$ species. The total conductivity is

$$\sigma = (p_{\text{int}} + p_{\text{non}}) \mu_h \cdot qz$$  \hspace{1cm} (13)

Therefore, we may rewrite as

$$\sigma = \sigma_{\text{int}} + \sigma_{\text{non}}$$  \hspace{1cm} (14)

To separate nonstoichiometric defect behavior in electrical conductivity, it is useful to represent total conductivity as the sum of all contributions:

$$\sigma = C + K pO_2^{1/n}$$  \hspace{1cm} (15)

where $C = \sigma_{\text{int}}$ and $\sigma_{\text{non}} = K pO_2^{1/n}$.
Figure 15 shows the dependence of conductivity on several integer values of $n$ ($n = 1$ to 8), along with experimental data at 700 and 1100°C (the large filled circles show the fitting examples). The data were well-represented in a linear plot $n = 6.0$. Figure 16 shows conductivity at temperatures between 700 and 1100°C, where $pO_2^{1/6}$ provides the best linear fit. From Eq. 10, the intercept yields the intrinsic conductivities ($\sigma_{\text{int}}$), which are a constant value at each temperature. Figure 17 shows that the log $\sigma_{\text{int}}$-versus-inverse-temperature data are not linear. This curvature may be explained by the temperature variation of the gap energy; however, the thermal gap obtained from this fit is $\approx 1.2$ eV. Gap energy varies with temperature in the case of an optical gap (Fig. 18). In the temperature range 700-1100°C, the optical gap ($E_{\text{gap}}$) varies from 1.3 to 1.6 eV. In general, optical gap energy is not higher than that of the thermal gap, based on the Frank-Condon principle.

Because conductivity follows a $pO_2^{1/6}$ dependence at each temperature and the mobility of holes is temperature-dependent, this suggests that conduction occurs by hole-hopping. If a thermally activated process is assumed for the hole migration,

$$\mu_h = \mu_{0,h} e^{-E_m/kT}$$  \hspace{1cm} (16)

where $\mu_{0,h}$ is constant and $E_m$ is the activation energy for migration of holes. The electrical conductivity from the normal conductivity equation, coupled with Eq. 16 yields

$$\sigma = \rho q \mu_{0,h} e^{-E_m/kT}.$$  \hspace{1cm} (17)

However, when the migration energy is known, a defect-formation energy can be calculated from the log slope (slope in Fig. 16)-versus-inverse temperature plot.

To calculate the mobility of holes, literature values at different stoichiometries were combined with the electrical conductivity data. When we assume that the ionic defects are totally ionized and the holes are the charge-compensating defects, hole mobility can be calculated by assuming that mobility is not a function of composition in the Cu$_2$O phase. With the normal conductivity equation modified as follows,

$$\mu = \Delta\sigma/\Delta p q = \Delta\sigma/[z \Delta x/V_{\text{cell}}] q$$  \hspace{1cm} (18)

*Peterson and Wiley and Bloem suggested a temperature-independent hole mobility, i.e., the hole migration energy, $E_m$, is close to zero.
where z and \( V_{\text{cell}} \) were defined in Table 2, the values of calculated hole mobilities at 900 and 1000°C are as shown in Table 4 and Fig. 19. The values are slightly higher at 1000°C. If we assume complete ionization of ionic defects and that the holes (formed as a charge-compensating defect) are localized in the normal copper sites, i.e., \( \text{Cu}^{+1} \) then becomes \( \text{Cu}^{+2} \), the calculated hole migration energy from the slope of Fig. 19 is 0.29 eV, according to Eq. 3.

3.5 Thermodynamic Considerations

For dilute-solution behavior, \( \Delta H_{\text{O}_2} \) may be related to the standard enthalpy of formation of nonstoichiometric defects. Phenomenologically, \( \Delta H_{\text{O}_2} \) is defined as the enthalpy change that accompanies the reaction described by
Fig. 16. Electrical conductivity vs. $pO_2^{1/6}$ at temperatures between 700 and 1100°C.

Fig. 17. $\log \sigma_{\text{int}}$ (in Fig. 16 of $pO_2 = 0$) vs. $1/T$ for calculated thermal gap based on slope of 1.2 eV for Cu$_2$O.
Table 4. Calculated hole mobilities for Cu$_2$O

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Calculated Hole Mobility (cm$^2$/V·s)</th>
<th>Ref. $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1173.16</td>
<td>0.827</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>0.891</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>0.594</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>1.069</td>
<td>8</td>
</tr>
<tr>
<td>1273.16</td>
<td>1.047</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>1.002</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>0.737</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>1.483</td>
<td>8</td>
</tr>
</tbody>
</table>

$^a$Reference number for the x values (Cu$_{201-x}$) used. $V_{cell}$ = unit cell volume [$V_0$ (at 298 K) = 77.833 x $10^{-24}$ cm$^3$] and thermal expansion coefficients were used $\alpha$ = 1.9 x $10^{-6}$/°C; $V(T)$ = $V_0$ (1 + $\alpha$T) used data in Ref. 16.

Limit $[O_2(g, 1 \text{ atm}) + 2/\delta \text{ Cu}_2\text{O}_{1+x} (s) = \text{ Cu}_2\text{O}_{1+x} + \delta(s)] ; \Delta H_{O_2}$ $\delta \rightarrow 0$  \hspace{1cm} (19)

where $x$ indicates the deviation from stoichiometry due to the excess oxygen in the lattice. One may consider the microscopic incorporation of oxygen into Cu$_2$O$_{1+x}$ by a defect mechanism involving doubly ionized oxygen interstitials and holes localized on copper ions. The microscopic equivalent to Eq. 19 can be written as

$O_2(g, 1 \text{ atm}) + 4 \text{ Cu}^{x+} \rightarrow 2 \text{ O}^{2-} + 4\text{ Cu}^{2+} ; \Delta H_{O_2}$  \hspace{1cm} (20)
The corresponding defect reaction for the formation of doubly ionized oxygen interstitials as the nonstoichiometric defect with each component in its standard state is

$$\text{Oi}^* + 2 \text{Cu}_{\text{i}} \rightarrow 2 \text{Cu}_{\text{o}}^x + \frac{1}{2} \text{O}_2(\text{g}) \quad \Delta H^o$$

(21)

where $\Delta H^o$ is the standard enthalpy for the reaction. Note that the reaction in Eq. 21 is similar to one-half the reverse of the reaction in Eq. 20. Thus, a consequence of dilute-solution behavior is that

$$\Delta H_{02} = -2 \Delta H^o.$$  

(22)

The cubic structure of cuprite (Cu$_2$O) is shown in Fig. 20. An oxygen interstitial is expected in a body-centered-cubic structure of Cu$_2$O, where the oxygen sublattice is open. The ionization state for interstitial oxygen is expected to be -2 because the normal charge of oxygen in both of the stable oxides (CuO and Cu$_2$O) is -2. Figure 21 depicts the log $\sigma_{\text{non}}$ versus log $pO_2$ for nonstoichiometric Cu$_2$O.

From the proposed nonstoichiometric defect reaction in Eq. 3, we can apply the quasichemical approach. The mass action constant and electroneutrality condition are given by

$$K_{\text{ma}} = [\text{Oi}^*][\text{h}^+]^2/pO_2^{1/2}$$  

(23)

$$2[\text{Oi}^{2+}] = [\text{h}^+]$$  

(24)
Fig. 20. Body-centered-cubic cell of Cu$_2$O; larger ions are oxygen and center "I" denotes oxygen interstitial position, which is open.

Fig. 21. Log $\sigma_{\text{non}}$ vs. log pO$_2$
Therefore, we can denote the concentration of holes as
\[
[h^-] = K_{ma}^{1/3} \cdot pO_2^{1/6}
\]
(25)

or, by combining the normal conductivity relation, we obtain
\[
\sigma_{\text{non}} \propto K_{ma}^{1/3} \cdot pO_2^{1/6}.
\]
(26)

Because
\[
K_{ma} \propto K_{th} = \exp \left( -\frac{\Delta G^o}{kT} \right)
\]
\[
= \exp \left( -\frac{\Delta H^o}{kT} \right) \cdot \exp \left( \frac{\Delta S^o}{k} \right),
\]
(27)

where \(K_{th}\) is the thermodynamic equilibrium constant, we obtain
\[
\sigma_{\text{non}} \propto \exp \left( -\frac{\Delta H^o}{3kT} \right) \cdot pO_2^{1/6}.
\]
(28)

If it is recognized that \(\sigma_{\text{non}} \propto [h^-] q \cdot \mu_{h^-}\), where the hole mobility is given by Eq. 11, we obtain
\[
\sigma_{\text{non}} \propto \exp \left( -\left(\frac{\Delta H^o}{3} + E_m\right)/kT \right) \cdot pO_2^{1/6}.
\]
(29)

For a defect mechanism of doubly ionized oxygen interstitials, \(O_i^*\), where the holes are localized at Cu sites as \(Cu^{+2}\) or \(Cu_{Cu'}\), the formation energy of 0.65 eV was calculated on the basis of an oxygen-pressure dependence of \(n = 6.0\), as shown in Fig. 22. At a constant temperature, \(\sigma_{\text{non}}\) is proportional to \(pO_2^{1/6}\).

![Fig. 22. Log slope (d\sigma/dpO_2^{1/6}) vs. 1/T for Cu_2O](image)
From Fig. 12 (a plot of log \( \sigma_{\text{non}} \) versus inverse temperature at constant oxygen pressure), this yields a slope \( (\Delta H^*/3 + E_m)/k = 0.628 \). The activation energy for hole motion, \( E_m = 0.29 \text{ eV} \), and the quantity, \( \Delta H^o \), is 1.01 eV; consequently, the standard oxygen formation enthalpy, \( \Delta H_{O2} \), is 2.02 eV, from Eq. 22. These thermodynamic quantities were calculated from model-based defect equilibria and can be compared with thermodynamic values measured directly.

Tretyakov et al.\(^6\) reported oxygen concentrations, as a function of temperature and \( p_{O2} \), obtained by high-temperature, solid-state coulometric titration. They analyzed the data by assuming that the deviation from stoichiometry, \( x \) (in Cu\(_2\)O\(_{1+x}\)), varies with \( p_{O2}^{1/4} \) dependence. We analyzed their data for the case where \( x \approx p_{O2}^{1/6} \). The fit based on our model, Fig. 23(a), is good. Log \( x \) versus log \( p_{O2} \) was replotted in Fig. 23(b) and 23(c).

### 3.6 Hole Mobility

To determine the mobility of holes, electrical conductivity and weight-change were measured simultaneously on thermally oxidized large-grain samples of nonstoichiometric Cu\(_2\)O. Sample temperature was varied and an inert atmosphere was made by flowing argon gas through the measuring system.\(^{27}\) The results are shown in Fig. 24. The calculated activation energy of 0.87 eV was obtained from the plot of log \( \sigma \) versus inverse temperature, and the monitored weight change is essentially zero. The calculated activation energy obtained by this method is higher than that determined under equilibrium conditions (0.628 eV). This suggests a somewhat different behavior in electronic transport properties in nonstoichiometric Cu\(_2\)O relative to other non–stoichiometric metal oxides such as Cr\(_2\)O\(_3\)\(^{27}\) or CeO\(_2\).\(^{29}\) In most metal oxides, activation energy determined under equilibrium conditions is higher than that obtained from a specimen with a fixed composition because the activation energy for conduction under equilibrium is the sum of migration energy and the energy of formation of the defect. However, the electronic transport properties in nonstoichiometric Cu\(_2\)O can be explained by two different mechanisms: when the material is in equilibrium with oxygen, the predominant electronic properties are controlled by the narrower gap, but when the composition is fixed and the temperature is varied, the electronic defect is controlled intrinsically and this manifests itself as a higher gap energy in nonstoichiometric Cu\(_2\)O.

Another method was also employed to confirm the thermodynamic quantities obtained from electrical conductivity as a function of temperature and \( p_{O2} \). Direct thermodynamic measurements were performed on copper oxide systems by setting up fixed compositions. Figure 25 is typical for the log \( \sigma \) and log \( p_{O2} \) versus inverse temperature obtained simultaneously at several constant compositions. The oxygen formation enthalpy (\( \Delta H_{O2} \)) and hole conduction energy (\( E_H \)) were calculated from the slopes in Fig. 25(b) and are represented in Fig. 26. In this
Fig. 23. (a) $pO_2^{1/n}$ vs. change of stoichiometry for two examples ($n = 6$ and $n = 4$): $n = 6$ gives better fit; (b) $\log x$ (in Cu$_2$O$_{1+x}$) vs. $pO_2^{1/6}$ fit for data found in Ref. 6, and (c) replot of (b) as $\log x$ vs. $\log pO_2$. 
Fig. 23. (Contd.)

\[10^4 X (X \text{ in } \text{Cu}_2\text{O}_{1+x})\]

Nonstoichiometry vs. \([pO_2 (atm)]^{1/6}\)

- Slope = \(2.89 \times 10^{-3}\)
  - \(T = 1000 \degree C\)

- Slope = \(2.17 \times 10^{-3}\)
  - \(T = 950 \degree C\)

Fig. 24. Simultaneous measurements of electrical conductivity and weight change in inert environment of argon gas

\[\text{Log Weight Change (\text{g/g})} - \text{Conductivity (ohm cm)}\]

\(E_H = 0.87 \text{ eV}\)
Fig. 25. Typical plots for results of simultaneous measurements of electrical conductivity and $pO_2$ for (a) constant composition measurement and (b) collected data plot for $\log$ conductivity and $\log$ $pO_2$ vs. $1/T$.
Fig. 26. Calculated oxygen formation enthalpy, $\Delta H_{O_2}$, and hole conduction energy, $E_H$, from slope data of Fig. 25(b).

figure, log $pO_2$ corresponds to the equilibrium composition at 994°C for each run. $\Delta H_{O_2}$ is $2.0 \pm 0.2$ eV and $E_H$ is $0.82 \pm 0.02$ eV. These results agree with the values obtained at a fixed composition when the temperature was varied by flowing an inert gas. However, at the lowest $pO_2$, $\Delta H_{O_2}$ decreased (Fig. 26); this may be attributed to the decomposition reaction $Cu_2O \rightarrow Cu + CuO$ and the subsequent oxidation of copper (i.e., $Cu + 1/2 O_2 \rightarrow CuO$) denoted by the dashed line in Fig. 14. The transition $pO_2$ values were obtained from Fig. 14. However, for the large-grain polycrystals of $Cu_2O$, the type of profile in Fig. 27 was barely detectable during pumping of oxygen while monitoring conductivity and $pO_2$.

The $CuO/Cu_2O$ phase transition is clearly evident in the temperature dependencies of EMF, the oxygen concentration in the gas phase (calculated from the ideal gas law, $pV = nRT$), and electrical conductivity in Fig. 28. The profiles for the temperature-dependent uptake and removal of oxygen are not identical in both phases. In $Cu_2O$ at low temperatures, the sample consumes more oxygen, but in the $CuO$ phase, which is stable at higher temperatures and high $pO_2$ values, oxygen absorption is lower. Electrical conductivity of the $CuO$ phase increases at higher temperatures. We could not obtain a fixed-composition measurement in the high-$pO_2$ case because the sample stoichiometry changes. The shape of the conductivity-versus-temperature curve near the transition region, Fig. 28(c), indicates the possibility of a metastable phase between $Cu_2O$ and $CuO$ in the Cu-O system.
Fig. 27. Electrical conductivity change with $pO_2$ associated with decomposition of $Cu_2O \rightarrow Cu + CuO$ during spontaneous pumping of oxygen from a thin-foil, thermally grown $Cu_2O$ specimen. For a large, thick, bulk sample, this trend is very weak.

4 SUMMARY

Oxidation of copper and electronic transport in thermally grown large-grain polycrystals of nonstoichiometric copper oxides ($Cu_2O$ and $CuO$) were studied at elevated temperatures. Oxidation rates were determined thermogravimetrically at temperatures from 350 to 1000°C. The temperature dependence of the oxidation rates, coupled with visual examination of the oxide films, suggested three different oxidation mechanisms: bulk diffusion at high temperatures, whisker formation with grain-boundary diffusion at intermediate temperatures, and surface reaction with whisker formation on the outer surface of the oxide at low temperatures.

Intensities of EDS spectra for various atomic valences of Cu were represented by the intensity ratio of the $Cu(l)$ to $Cu(K\alpha)$ transition. There is no significant difference in the ratio for $Cu$ and $Cu_2O$, but the values decreased for copper in higher valence state.

The electrical conductivity of nonstoichiometric $Cu_2O$ exhibits p-type behavior, but in $CuO$ only intrinsic behavior was observed. However, electronic transport in nonstoichiometric $Cu_2O$ was reconsidered in terms of both intrinsic and nonstoichiometric defects owing to reduction/oxidation processes. The electrical conductivity of $Cu_2O$ exhibited a 1/6-power dependence on the oxygen partial pressure, i.e., $\sigma_{non} = K pO_2^{1/6}$. 
Fig. 28. Cu$_2$O/CuO phase transition in terms of (a) variation of EMF vs. temperature, (b) variation of oxygen concentration in gas phase, and (c) electrical conductivity variation during transition
Calculated values for the enthalpy of formation of oxygen ($\Delta H_{\text{O}_2}$) and the hole conduction energy ($E_H$) at constant composition for nonstoichiometric Cu$_2$O are $2.0 \pm 0.2$ eV and $0.82 \pm 0.02$ eV, respectively.

ACKNOWLEDGMENTS

The authors thank C. L. Wiley for making and supplying the large-grain-size cuprous polycrystals, and for electrical conductivity data that were used in a previous paper (Ref. 13).

REFERENCES


Distribution for ANL-91/27

**Internal:**
- S. A. Borys
- H. Drucker
- T. F. Kassner
- C. A. Malefyty
- K. Natesan
- J. H. Park (10)
- D. Schmalzer
- W. J. Shack
- C. E. Till
- TIS Files (3)
- R. W. Weeks
- ANL Patent Dept.
- ANL Contract File
- T. F. Kassner
- H. Drucker
- D. Schmalzer
- W. J. Shack
- C. E. Till
- TIS Files (3)
- R. W. Weeks
- ANL Patent Dept.
- ANL Contract File

**External:**
- DOE-OSTI, for distribution per UC-400 (27)
- ANL Libraries (2)

**DOE Chicago Operations Office:**
- Manager  F. Herbaty
- D. L. Bray
- D. T. Goldman
- A. DasGupta

**Materials and Components Technology Division Review Committee:**
- H. Berger, Industrial Quality, Inc., Gaithersburg, MD
- M. S. Dresselhaus, Massachusetts Institute of Technology, Cambridge, MA
- S. J. Green, Electric Power Research Institute, Palo Alto, CA
- R. A. Greenkorn, Purdue University, West Lafayette, IN
- C.-Y. Li, Cornell University, Ithaca, NY
- P. G. Shewmon, Ohio State University, Columbus
- R. E. Smith, Electric Power Research Institute, NDE Ctr., Charlotte, NC

**U.S. Department of Energy, Washington:**
- Office of Fossil Energy:
  - D. J. Beecy
  - J. P. Carr
  - H. Feibus
  - G. Rudins
  - T. B. Simpson
- Office of Conservation:
  - J. J. Brogan
  - J. J. Eberhardt
  - J. Eustis
  - E. W. Gregory II
  - M. E. Gunn, Jr.
  - S. M. Wolf
- Basic Energy Sciences, Materials Science Division:
  - J. B. Darby
  - R. J. Gottschall

**DOE Morgantown Energy Technology Center:**
- Director

**DOE Oak Ridge Operations Office:**
- Manager  E. E. Hoffman
DOE Pittsburgh Energy Technology Center:

Director

Oak Ridge National Laboratory:

R. A. Bradley       R. R. Judkins

Other Government – University – Industry:

S. J. Dapkunas, National Institute of Standards and Technology, Gaithersburg, MD
D. Doughty, Sandia National Laboratories
D. W. Keefer, EG&G IDAHO, Inc., Idaho National Engineering Laboratory
F. S. Pettit, University of Pittsburgh, Dept. of Materials Science and Engineering, Pittsburgh, PA
K. M. Prewo, United Technologies Research Center, East Hartford, CT
R. A. Rapp, Ohio State University, Columbus
A. Schwanzkopf, National Science Foundation, Washington, DC
R. M. Spriggs, National Research Council, Washington, DC
J. Stringer, Electric Power Research Institute, Palo Alto, CA
K. M. Zwilsky, National Materials Advisory Board, National Research Council, Washington, DC