

Surface Energy of Copper as a Function of Oxygen Activity

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Surface energies of copper at 1027°C were determined as a function of oxygen fugacity. The value of the surface energy was 1.49 J/m² below 10⁻¹⁸ N/m² oxygen and decreased linearly from 10⁻¹⁸ to 10⁻¹¹ N/m². The region of linear decrease fitted the Gibbs adsorption isotherm and gave a surface coverage of 0.24 monolayers of oxygen. The surface energy apparently increased with oxygen fugacity in the range from 10⁻¹¹ to 10⁻⁷ N/m², but this was associated with effects introduced by a precursor oxide on creep rate rather than a true effect on surface energy.

INTERFACIAL energies are strongly influenced by impurities. The effect of oxygen pressure on the surface energy of copper is the subject of this study.

Gibbs¹ treated the thermodynamics of interfaces and derived a formal definition of the surface energy γ in terms of the variation of the Helmholtz free energy F of a system with surface area A at constant numbers of atoms of the i species, n_i , volume, V , and temperature, T ;

$$\gamma = \left(\frac{\partial F}{\partial A} \right)_{n_i, V, T} \quad [1]$$

The combined statement of the first and second laws of thermodynamics in the case of surface terms yields the Gibbs adsorption equation,

$$d\gamma = -SdT - \sum_i \Gamma_i d\mu_i \quad [2]$$

where S is the surface excess entropy per unit area, Γ_i is the surface excess concentration of the i th species per unit area, and μ_i is the chemical potential of the i th species.

For a system consisting of a metal surrounded by a surface active gas, oxygen, at pressures sufficiently low that the fugacity of the gas is equal to its partial pressure, the chemical potential is given by $\mu_o - \mu_o^0 = -kT \ln P_{O_2}^{1/2}$ where k is Boltzmann's constant and μ_o^0 is the standard state chemical potential. The Gibbs adsorption equation thus becomes

$$d\gamma = -SdT - (kT\Gamma_O/2) d \ln P_{O_2} \quad [3]$$

where Γ_O is the surface excess of oxygen atoms at the interface. At constant temperature the surface energy varies linearly with the logarithm of the gas pressure and this dependency should persist until a new phase forms.

The surface energy of copper was first determined in 1948 by Udin, Shaler, and Wulff.² They obtained a value of 1.37 J/m² at the melting point. However, they failed to correct their creep data for the presence of grain boundaries and later when Udin³ made the required corrections their value became 1.65 ± 0.10 J/m².

The surface energy of a metal near its melting point

is usually 20 to 30 pct greater than that of its liquid. Several reported values however, seem to be noticeably low, such as that of Hayward and Greenough⁴ who studied nickel. This led McLean and Hondros to study variations with oxygen pressure in the surface energies of copper⁵ and iron,⁶ and Stickley⁷ to do the same with nickel. These authors found that at extremely low oxygen pressures the surface energy was independent of oxygen pressure, indicating a metal surface which was clean relative to oxygen. However, at higher oxygen pressures the surface energy was found to vary linearly with pressure, as predicted by the Gibbs' adsorption isotherm, until pressures were reached where the bulk oxide became stable, whereupon the adsorption isotherm showed a discontinuity.

In Fig. 1 the Cu-O adsorption isotherm found by McLean and Hondros⁵ at 927°C is displayed. The discontinuity in the adsorption isotherm occurred at oxygen pressures five to six orders of magnitude below the dissociation pressure of the stable oxide. Hondros and McLean⁸ proposed that a precursor oxide formed prior to bulk oxide stability. This result can be justified thermodynamically if the metal-vapor interfacial

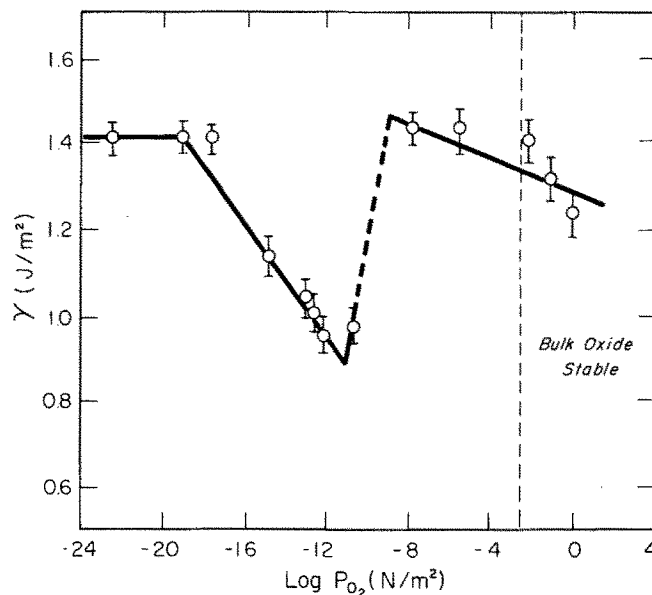


Fig. 1—Variation of the surface energy of copper with oxygen pressure at 927°C according to McLean and Hondros.⁵ Dashed vertical line represents the dissociation pressure of cuprous oxide.

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energy is greater than the sum of the metal-precursor oxide and precursor oxide-vapor interfacial energies. The thinner the precursor oxide layer the greater would be the effects of these interfacial energies on the formation of the precursor oxide. Thus, if there is a net release of interfacial energy on formation of a precursor oxide then this reaction is thermodynamically possible. Some indication of such an effect for nickel was found by Stickle.^{7,9}

Buttner, Funk, and Udin¹⁰ examined the effect of oxygen pressure on the surface energy of silver and did not find evidence of any precursor oxide in this system. Thus only Hondros and McLean have performed studies which exhibited such behavior over a wide range of pressure, and then only in the copper system. Hence, a subsidiary purpose of this study was to check the results of McLean and Hondros data using a highly accurate oxygen controlling system but with a different vapor phase composition to determine whether vapor phase constituents other than oxygen may have influenced their results. The present work employed controlled low partial pressures of oxygen in a residual 0.1 N/m² argon atmosphere.

EXPERIMENTAL PROCEDURES AND TECHNIQUES

The wires used were of 99.999 pct copper and of 25.4 μ m diam. Wire was obtained from A. D. Mackay, Inc., New York, New York. The wires were marked in 2 cm gage lengths with a razor blade, cleaned in acetone and rinsed in methanol. Appropriate weights added below each gage length yielded a set of specimens some of which had weights below the midpoint of their gage lengths greater than that required to achieve zero creep while others had weights less than the zero-creep weight. These specimens were then suspended on an alumina bar. The alumina bar was raised and lowered on a platinum chain.

The temperature in this study was 1027°C \pm 2°C. This temperature was maintained by a proportional controller responding to a platinum vs platinum-10 pct rhodium thermocouple calibrated with a gold filament. The controller operated a relay which supplied either 90 or 100 pct of the applied voltage from the power-stat and thus a constant temperature zone of 5 to 6.5 cm was maintained in the furnace.

An inert argon atmosphere was used to prepare the system for operation. First the system was evacuated by a mechanical pump and then argon, passed through a liquid nitrogen trap, was released into the system. This process was repeated several times and the system was isolated following the final evacuation to 0.1 N/m² residual argon pressure.

The oxygen control system developed by Rapp *et al.*,¹¹ utilizing a zirconia electrolyte with pumping and control electrodes and a special electronic control device, Quartec IV, has been described in detail elsewhere (Refs. 9, 11, and 12). In particular, as in the preceding paper,⁹ the reference electrode voltage, which is the measure of the oxygen fugacity in the system, was constant to within 0.1 pct during the course of a given experiment. Some comment is in order with respect to the lowest oxygen fugacities achieved here, however, an equivalent of 10⁻²⁰ N/m², which corresponds to an oxygen content of one molecule per liter in a pure oxy-

gen atmosphere. Rapp *et al.*¹¹ presented detailed data for equivalent pressures down to 10⁻¹¹ N/m² but some data down to 10⁻¹⁵ N/m². As mentioned by them, even at these latter equivalent pressures, what is actually being controlled is the oxygen fugacity or chemical potential, determined by H₂O/H₂ and CO₂/CO ratios in the (ppm) residual gas impurities in the argon rather than by the oxygen partial pressure, *per se*. The same situation holds in the work of McLean and Hondros,⁵ for example, where equivalent pressures down to 10⁻²³ N/m² were achieved by directly controlling the H₂O/H₂ ratio. Here, the same control via residual gas impurities as with the work of Rapp *et al.*¹¹ is attained: the justification being that the reference voltage did stabilize to a constant value within 7 pct of the set pump voltage at these low oxygen fugacities, the same variation as obtained in the work of Rapp *et al.*¹¹

Following the final evacuation of the system, the Quartec IV controller was turned on and when the desired oxygen pressure was attained the specimens were lowered into the hot zone for about 30 min. They were then raised into the glass housing above the zirconia tube and the gage lengths were checked *in situ* through a glass extension with a Gaertner micrometer slide cathetometer. After this initial annealing period the specimens were creep tested for periods of 40 to 50 h and the cumulative strain was determined at the end of each of these periods.

The estimated thermal rise time based on heat flow calculations gives a completely negligible error in the strain-time curves compared to the actual scatter of the data. On the basis of 1 ppm residual gas impurity and 0.1 N/m² total pressure, the relaxation time for one monolayer of residual gas to strike the specimens is 1 h, so this may have introduced up to a 3 pct transient effect in the experiments where oxygen influenced the rate. The number of grains in each gage length was also counted. At the end of a complete testing period, which involved 4 or 5 of the shorter creep testing periods, the weights below the midpoints of each gage length were determined to \pm 0.1 mg.

Data analysis involved determining linear strain rates from plots of the cumulative strain vs time. Then from plots of strain rate vs load the zero creep weight w_0 for a given oxygen pressure could be found. This weight w_0 was then used to determine the surface energy γ from the well known equation^{13,14}

$$w_0 = \pi r \gamma - (n/l) \pi r^2 \gamma_g \quad [4]$$

where r is the wire radius, n the mean number of grains per length l , which is the gage length, and γ_g is the grain boundary energy.

RESULTS AND DISCUSSION

The experimental techniques used make testing to oxygen pressures as low as 10⁻²⁰ N/m² (10⁻²⁵ atm) feasible.¹¹ In the present research experiments were conducted at 7.4 \times 10⁻²⁰, 1.3 \times 10⁻¹⁸, 8.1 \times 10⁻¹⁴, 2.8 \times 10⁻¹², 6.3 \times 10⁻¹⁰, 3.1 \times 10⁻⁷, and 5.3 \times 10⁻⁴ N/m² of oxygen and a temperature of 1027°C \pm 2°C.

Nabarro-Herring creep theory predicts that creep rates are proportional to applied loads. Fig. 2 shows a cumulative strain vs time plot. As seen in Fig. 2, after a primary creep transient, a steady-state creep

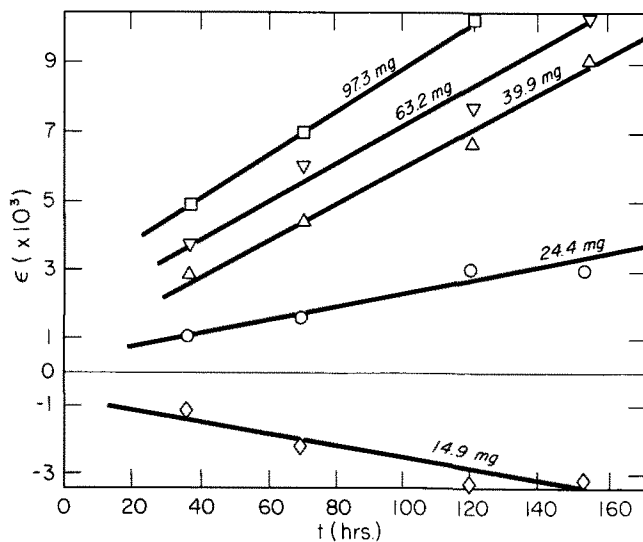


Fig. 2—Cumulative strain (ϵ) vs time (t) at 2.8×10^{-12} N/m² oxygen pressure.

Table I. Surface Energies of Copper at Several Oxygen Pressures

Oxygen Pressure, N/m ²	Surface Energy, (J/m ²)
7.4×10^{-20}	1.480 ± 0.045
1.3×10^{-18}	1.492 ± 0.020
8.1×10^{-14}	1.342 ± 0.010
2.8×10^{-12}	1.132 ± 0.090
6.3×10^{-10}	0.997 ± 0.083
3.1×10^{-7}	1.334 ± 0.109
5.3×10^{-4}	1.324 ± 0.073

rate was achieved. No trend in transient behavior as a function of oxygen fugacity was observed: the data exhibited a normal transient with decreasing strain rate whether the strain was tensile or compressive, typical of microcreep data of this type.^{2,4,5,13,14} As indicated in Table I, the plots in Fig. 2 are representative of those with the highest experimental scatter among the data sets. Complete data are presented in Ref. 12. This figure is for an oxygen pressure of 2.8×10^{-12} N/m². The steady state creep rates increase with increasing loads.

Fig. 3 presents the steady state creep rate vs load plots obtained from data such as that of Fig. 2. In these plots the high load points are seen to fall below the extrapolated line based on points near the zero creep value. This trend held for data in the present work and elsewhere as discussed below. Hence the highest load points were excluded in the least squares determination of the zero creep load. The zero creep weight obtained from this figure was used in Eq. [4] to obtain the surface energy under the given environmental conditions. The values of the surface energy of copper resulting from this analysis are listed in Table I. In order to calculate the surface free energy it was necessary to know n/l and the grain boundary energy to surface energy ratios. The value of n/l was determined to be 70.9 cm⁻¹ with an accuracy of 5 pct. The ratio γ_g/γ was taken to be the value 0.326 determined at 1030°C by McLean.¹⁵

Fig. 4 depicts the surface energy of copper as a function of $\log P_{O_2}$ at a temperature of 1027°C. There is a region below 10^{-18} N/m² which does not vary with

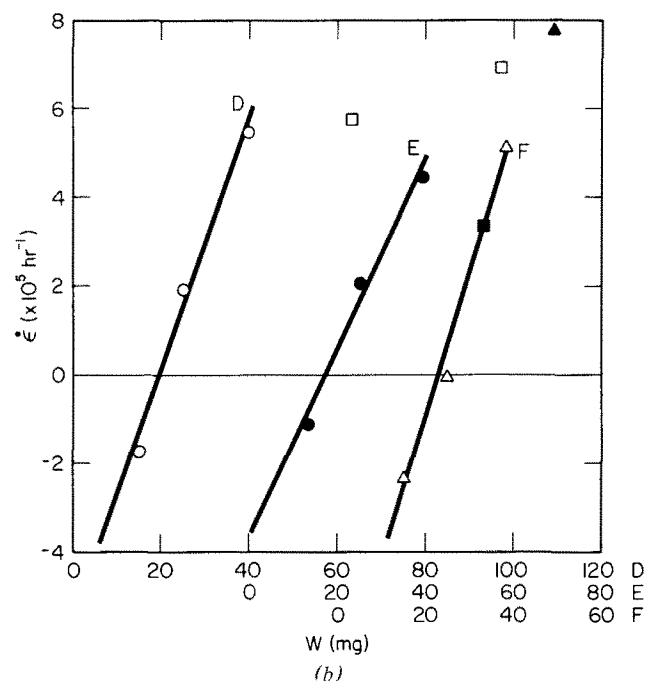
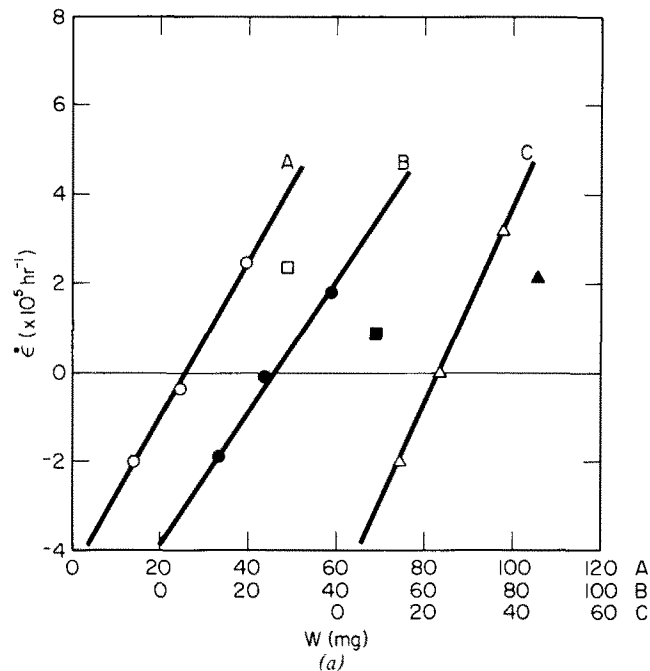


Fig. 3—Strain rate ($\dot{\epsilon}$) vs load (w): (a), at 7.4×10^{-20} N/m² oxygen fugacity (open circles, squares, curve A), at 1.3×10^{-18} N/m² (closed circles, squares, curve B), and at 8.1×10^{-14} N/m² (triangles, curve C); (b), at 2.8×10^{-12} N/m² (open circles, squares, curve D), at 6.3×10^{-10} N/m² (closed circle, squares, curve E), and at 3.1×10^{-7} N/m² (triangles, curve F).

oxygen pressure, indicating a metal surface free of oxygen. Then linear behavior following the Gibbs adsorption isotherm behavior occurs up to 10^{-11} N/m² oxygen where the same discontinuity observed by McLean and Hondros⁵ is encountered. The McLean-Hondros result of Fig. 1 is also shown in Fig. 4 and is seen to agree quite well with our data. Indeed the shift of the sloped lines to higher oxygen pressures by about an order of magnitude in our work compared to that of McLean and Hondros is consistent with the shift of the dissociation pressure by about the same

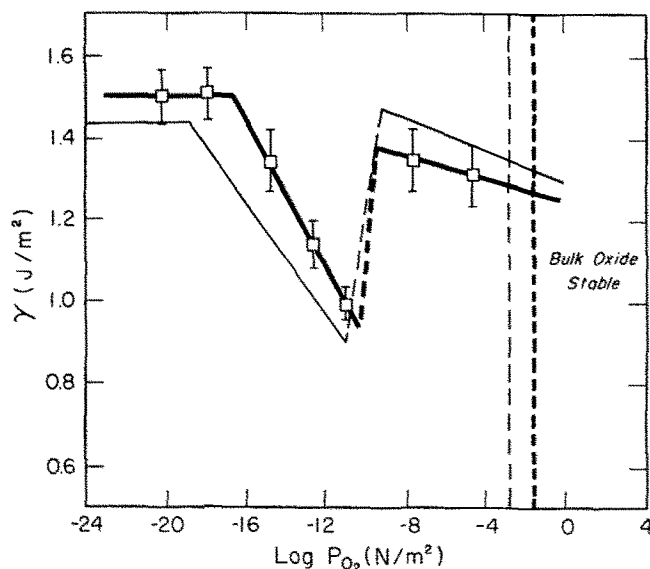


Fig. 4—Variation of the surface energy of copper with oxygen pressure at 1027°C according to the present work (heavy lines) and at 927°C according to Hondros and McLean² (light lines). Dashed vertical lines represent the dissociation pressure of cuprous oxide.

amount with the increase in temperature.

From Eq. [3] the surface excess of oxygen at constant temperature can be calculated using the slope of the Gibbs adsorption isotherm.

$$-\Gamma_O = \frac{2}{kT} \frac{d\gamma}{d \ln P_{O_2}} \quad [5]$$

For a decrease of 0.08825 J/m² in surface energy per tenfold increase in oxygen pressure, the surface excess of oxygen on copper is 4.27×10^{18} atoms/m² which corresponds to 0.24 monolayers of oxygen on a (111) plane. This compares favorably with the 0.22 value obtained by McLean and Hondros.⁵

In the region of oxygen pressure greater than 10^{-11} N/m², the surface energies are probably only apparent. As discussed by McLean and Hondros,⁵ the increase is thought to be associated with the formation of a precursor oxide. This oxide could either lead to a decrease in creep rate because of its high viscosity or because the surface energies involved are now those of the precursor oxide. Some independent evidence for a precursor oxide has appeared as this report was being prepared.²⁴

The value of the surface energy at 1027°C of 1.49 ± 0.07 J/m² for the oxygen-free surface compares well with the value of 1.42 ± 0.03 J/m² at 972°C determined by McLean and Hondros.⁵ The latter authors were puzzled that their result was lower than the average value 1.73 J/m² of earlier work,^{2,3,16,17} in the same temperature range, as computed by Inman and Tipler,¹⁴ but they noted that their lower value gave better agreement with expectation deduced from the liquid copper surface energy at the melting point. In at least one instance, we believe that the higher value¹⁴ is associated with the high load creep rate diminution observed in the present work and elsewhere. Inman and Tipler¹⁴ present otherwise unpublished data of McLean and Tipler¹⁶ for microcreep of copper wire at 950°C which

gave a value of $\gamma = 1.77$ J/m². Recalculation from their graph excluding the high load points give 1.53 J/m² in much better agreement with the present work and that of McLean and Hondros.⁵ Udin³ recalculated a value of 1.65 ± 0.10 J/m² at 1080°C for wire creep results;² he used a value of $n/l = 80 \pm 10$ cm⁻¹ determined in an experiment separate from the creep work. The difference of this value of n/l from the other cases may account for the discrepancy in γ values. Pranatis and Pound,¹⁷ for microcreep of copper foils, found 1.66 J/m² at 1024°C. Hence, the high load correction brings all of the above results into somewhat closer agreement and gives an overall average from all measurements of 1.55 J/m².

The trend of creep rate falling below the linear plot through the zero creep rate point was observed in the present work and in other cases,^{2,7,14,16} for both tensile loading and for compressive loading by the surface energy. Roughly, the effect appears for loads whose absolute value differs from the zero creep load by more than 80 pct. For data in a smaller load range,⁵ no such deviation is observed. At much higher loads,¹⁸ the creep rate undergoes a transition to power law creep with a stress exponent of 3 or greater so that deviation in the opposite sense (positive curvature in a creep rate-stress plot) is eventually observed. We believe that these results are understandable mechanistically.

Seidman and Balluffi¹⁹ have shown that dislocations are not perfect sinks for vacancies under moderate supersaturations. In addition, the observation²⁰ of a Bardeen-Herring source, grain-boundary dislocation within a grain boundary implies that boundaries are also not perfect sinks. Well known principles of competition between interface control and diffusion control then indicate that for a process of this type, which the classical Herring-Nabarro creep model is, local equilibrium boundary conditions are nearly obtained for small deviations from local equilibrium, *i.e.* for loads near the zero-creep load. For larger deviations, however, local equilibrium cannot be maintained at the grain boundary, part interface control obtains, and the rate drops below the prediction of the classical model. Eventually, at sufficiently large loads, dislocation generation intrudes into the process, and changes the mechanism to a power-law type.¹⁸

A final point relates to the specific agreement with the Herring-Nabarro creep equation, which can be expressed as²¹

$$\frac{d\dot{\epsilon}}{d\sigma} = \frac{B D \Omega}{2 k T L r} \quad [6]$$

where B is a constant²¹ equal, in the present case, to 12.3, D is the diffusivity, Ω is the atomic volume, and L is the axial length of an average grain. With the value for D given by Maier and Nelson,²² the computed value from Eq. [6] is $d\dot{\epsilon}/d\sigma = 1.44 \times 10^{-13}$ m²/Ns. The average slope of the oxygen-free curves A and B of Fig. 3 is $d\dot{\epsilon}/d\sigma = 9.36 \times 10^{-14}$ m²/Ns (± 10 pct). Expressed as a ratio of D/D_{exp} , where D_{exp} is the value deduced from creep rates and Eq. [6] the ratio is found to be 1.54. This can be compared with similar data for Co, Ni and Fe, respectively, which gave ratios²³ of 7.8, 10.3 and 6.5. Hence, agreement with the Herring-Nabarro theory is good.

SUMMARY

1) The surface energy of copper at 1027°C is constant below 10^{-18} N/m² oxygen pressure and decreases following the Gibbs adsorption isotherm from 10^{-18} to 10^{-11} N/m² oxygen pressure. The surface energy apparently increases in the range from 10^{-11} to 10^{-7} N/m² oxygen pressure but this probably reflects control of microcreep by factors other than surface energy.

2) The oxygen-free value of the surface energy is 1.49 J/m².

3) The surface energy of copper falls 0.08825 J/m² for each tenfold increase in the oxygen pressure in the region of the Gibbs adsorption behavior, corresponding to a surface coverage of 0.24 monolayers of oxygen.

4) In agreement with the work of McLean and Hondros,⁵ a discontinuity occurs in the Gibbs adsorption isotherm for the Cu-O system at an oxygen pressure of about 10^{-11} N/m², well below the region of bulk oxide stability.

5) The creep rates agree well with the Herring-Nabarro theory. Deviations from a linear strain rate-stress plot at high loads are associated with some interface control intruding upon the classical diffusion process.

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