JOURNAL OF MATERIALS SCIENCE 5 (1970) 374–378

Inhibition of Diffusion Creep in Copper by Dissolved Oxygen

E. D. HONDROS, C. R. LAKE
Division of Inorganic and Metallic Structure, National Physical Laboratory, Teddington, Middx, UK

It is proposed that under certain conditions, diffusion creep may be interface-controlled. Evidence is presented for copper with oxygen in solid solution, in which conditions oxygen chemisorbs at interfaces, and reduces their effectiveness as sources and sinks for vacancies, thereby slowing down diffusion creep. In addition, in conditions where the surface oxide is stable, inhibition of diffusion creep is even more pronounced.

1. Introduction

Diffusion creep or Herring-Nabarro creep plays an important rôle in sintering kinetics. It is also a mode of plastic deformation for metals and alloys held in service conditions of low stress and high temperature, such as the magnesium alloys used in nuclear fuel element cans [1]. In recent work in this laboratory, it was observed that when copper is held at high temperature in conditions where the oxide is unstable, the rate of diffusion creep is sensitive to the very low partial pressures of oxygen in the ambient atmosphere. In the following, we discuss these observations within the broad context of means of controlling diffusion creep.

Whereas in most diffusion creep phenomena, it is assumed that diffusion through the lattice is rate-controlling, it is proposed here that under certain conditions, interfaces may be rate-controlling. In particular, the interfacial adsorption of certain species can retard the generation or absorption of vacancies, thus reducing the diffusion creep rate.

2. Experiments and Observations

The experimental procedures for studying diffusion creep in thin foils or wires have been recently reviewed by Jones [2]. In essence, specimens with a large surface to volume ratio are subjected to low stresses (less than 10^6 dynes cm^{-2}) at high temperature, and strain rates are measured. In our work, measurements of extension or of negative creep (contraction) of the foils are carried out *in situ*, and in conditions of rigidly controlled atmospheres [3]. A wide range of oxygen potential is achieved, here from $pO_2 = 10^{-27}$ atm to $pO_2 = 10^{-5}$ atm by manipulating a range of mixtures of H_2O, argon and H_2 and carefully varying the controlled dew point. From this the equivalent pO_2 is computed by referring to the appropriate gas phase equilibrium equations.

The main features of the results are shown in fig. 1. Firstly, with the low effective stresses used here, all creep relations are of the general form $\dot{\epsilon} = A\sigma_e$, which is the condition for viscous deformation. In the above, if σ_0 is the stress equivalent of the surface tension, $\sigma_e = \sigma - \sigma_0$, for $\sigma > \sigma_0$ (extension of specimen) and $\sigma_e = \sigma_0 - \sigma$ for $\sigma_0 > \sigma$ (contraction of specimen). The additional feature of the creep behaviour that drew our interest is also demonstrated: thus, as an example, in experiments B (at an oxygen potential of 10^{-6} atm) the creep rate at a given stress is about an order of magnitude lower than in experiments A, conducted at the extremely low oxygen potential of 10^{-25} atm. As the results in the table show, on specimens of a similar grain size (0.55 mm), except for the first value, there is a broad trend of decreasing creep sensitivity to stress with increasing oxygen potential of the ambient atmosphere.

3. Discussion

3.1. Apparent Volume Diffusivities

In earlier studies in ferrous systems [3], it was demonstrated that certain solutes may alter appreciably the self-diffusivity of the solvent. The first possibility that we should examine then, is that the copper self-diffusivity is retarded by

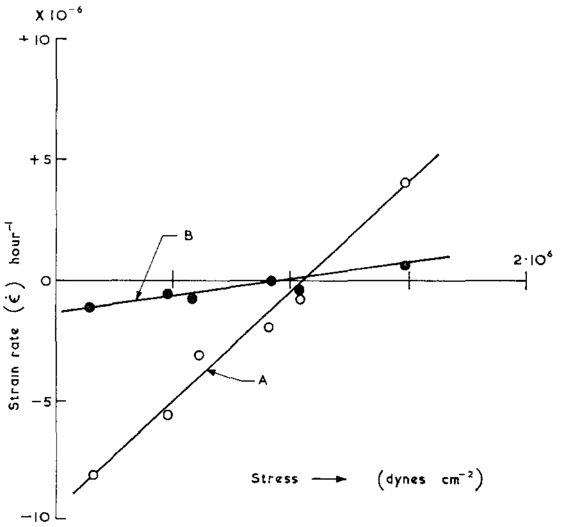

Figure 1 Viscous creep of copper at 927° C in an atmosphere of low pO_2 (relation A) and high pO_2 (relation B).

oxygen in solid solution.

Self-diffusion coefficients are calculated assuming uninhibited Herring-Nabarro creep. Applying the relation appropriate to thin foils [3], namely

$$D = \frac{\dot{\epsilon}}{\sigma} \cdot \frac{at\mathrm{R}T}{\Omega B}$$

where $\dot{\epsilon}$ is the strain rate, σ the stress, a the grain size, t the thickness of the foil, Ω the atomic volume, B a dimensionless parameter(= 10.2 in this case) and RT have the usual meaning. The computed self-diffusivities of copper are shown

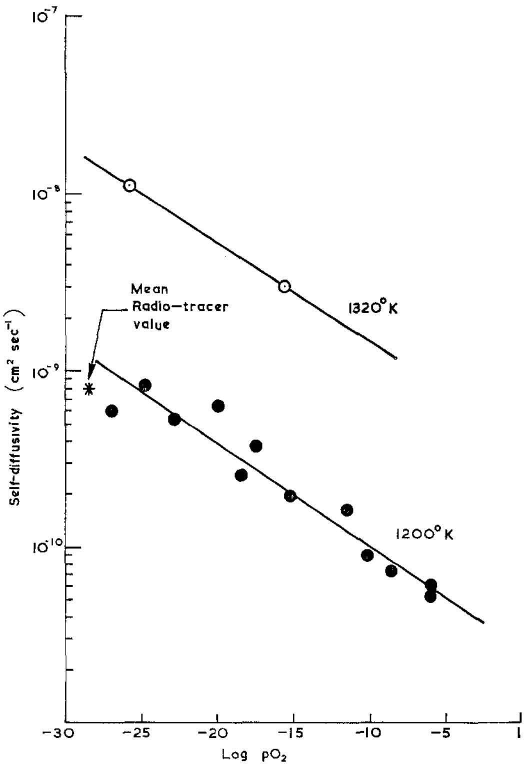

Figure 2 Self-diffusivity of copper as a function of oxygen potential of the atmosphere: the self-diffusivities have been deduced on the assumption that unimpeded diffusion creep obtains.

in fig. 2 as a function of pO_2. At very low oxygen potentials, there is excellent agreement between

TABLE

Experiment	$\frac{\dot{\epsilon}}{\sigma}$ (cgs units)	Oxygen potential (atm)	Temperature (°C)	Calculated diffusivity (cm² sec⁻¹)
75	25.7×10^{-15}	1.0×10^{-27}	927	5.3×10^{-10}
65	50.6×10^{-15}	1.6×10^{-25}	927	8.2×10^{-10}
66	30.7×10^{-15}	1.6×10^{-23}	927	5.3×10^{-10}
67	23.9×10^{-15}	1.1×10^{-20}	927	6.3×10^{-10}
70	8.5×10^{-15}	3.3×10^{-19}	927	2.6×10^{-10}
68	12.3×10^{-15}	3.5×10^{-18}	927	3.8×10^{-10}
69	6.5×10^{-15}	9.0×10^{-16}	927	2.0×10^{-10}
71	14.0×10^{-15}	2.5×10^{-13}	927	1.8×10^{-10}
72	7.2×10^{-15}	7.1×10^{-11}	927	8.9×10^{-11}
73	5.8×10^{-15}	2.3×10^{-9}	927	7.3×10^{-11}
74	4.1×10^{-15}	1.0×10^{-6}	927	5.2×10^{-11}
76	2.9×10^{-15}	1.0×10^{-6}	927	6.2×10^{-11}
64		1.1×10^{-23}	983	3.2×10^{-8}
81		1.3×10^{-26}	1047	1.1×10^{-8}
82		2.9×10^{-16}	1047	3.0×10^{-9}

the present results and self-diffusivities derived from published radio-tracer diffusion parameters [4]; however, with increasing pO_2, this interpretation implies that there is a consistent decrease in self-diffusivity with increasing pO_2. A similar trend is shown for the two values at 1320° K.

This interpretation seems highly implausible when one considers that oxygen is not very soluble in copper. Thus Pastorek and Rapp [5] have recently shown that the maximum solubility of oxygen in copper at 1200° K is 7.8×10^{-5} atoms of oxygen per atom of copper. The equilibrium constant in Sievert's Law can be derived by noting that the maximum solubility corresponds to the oxygen potential where bulk oxidation commences, which in the present work is $\log pO_2 = -7.14$. Thus at 1200° K, the oxygen solubility in copper in terms of the partial pressure of oxygen can be described by $[O] = 0.29\sqrt{pO_2}$. Hence in the present conditions, oxygen solubilities are extremely low.

Examining this point further, suppose that oxygen enters substitutionally in the copper lattice; then Lidiard's theory [6] on the effects of solutes on the self-diffusivity of the solvent may be applied. This assumes short-range interactions between solute atoms and vacancies and leads to a linear dependence of solvent diffusivity $D_{(c)}{}^1$ on concentration, c. For the present system, it may be shown to take the form

$$D_{(c)}{}^1 = D_{(0)}{}^1(1 + 1.88 \times 10^5 C)\ ,$$

where the relevant diffusion data are obtained from [4] and [5] and the correlation factor is taken as 0.5, which seems reasonable according to Lidiard's calculations. Thus, in principle, oxygen should enhance the copper self-diffusivity. If, on the other hand, oxygen enters interstitially as it is claimed [5], theory would predict that solvent diffusivity is either unaffected or enhanced.

3.2. Inactivation of Vacancy Sources

Retarded diffusivity cannot explain the observations. The possibility that adsorbed impurities may inactivate boundary sources of atoms or vacancies was suggested in an earlier publication [3]. The present work supports this.

This can be best seen by plotting the results for 1200° K in terms of the viscosity coefficient ($\eta = \partial\sigma/3\partial\dot{\epsilon}$) as a function of the oxygen potential of the atmosphere. This is shown in fig. 3. Concurrent work [7] in this laboratory on the adsorption of oxygen on copper has permitted us to characterise three physico-chemical regimes over this range of pO_2: a clean surface regime, a chemisorption range and a range of stable oxide formation – these are indicated in fig. 3. In general, the viscous behaviour of copper reflects the presence of these regimes. The low viscosities measured in the regime I correspond very closely to values predicted from the equation $\eta = at\mathrm{R}T/3\Omega BD$, by applying published diffusivity data. All values here fall in the range 0.6×10^{13} to 1.3×10^{13} poise. In regime II the viscosity increases by an order of magnitude and in III, it continues to rise steeply.

The interesting feature of this work is the behaviour in regime II. Recently it has been shown [7] that on copper surfaces under these conditions, there exists strongly chemisorbed oxygen at a coverage of about a quarter of a monolayer. It was also shown that there is a marked preference for occupation of sites at monatomic ledges. These are the surface features where vacancies are expected to be emitted or absorbed. It is proposed that the adsorbed oxygen inactivates these surface sites, thereby making it energetically more difficult for vacancies to pass through the surface. In a similar way the efficacy of grain-boundaries as vacancy sources should be affected by strongly adsorbed species. Adsorption of oxygen to copper grain-boundaries has not been measured, however, our experience to date provides no exception to the rule that species which are surface active also segregate to grain-boundaries. Thus all interfaces, both external and internal, that constitute the sources or sinks for vacancies in the diffusion creep process, will react in the same way to the presence of adsorbing species.

In the case of regime III, the oxide Cu_2O is stable according to thermochemical data. Thus, the very noticeable effect of suppression of diffusion creep is related to the presence of a continuous film of oxide on the surface which acts as a barrier to vacancy flow. The latter effect has been demonstrated by Harris and Masters [8] on zinc and magnesium, in which a continuous oxide film acted as a trap to quenched-in vacancies. In addition, in this regime, one would expect some oxide particles at grain-boundaries. This would correspond to the situation recently studied by Harris *et al* [9], where precipitates at grain-boundaries are shown to reduce diffusion creep, this being attributed to the particle/matrix

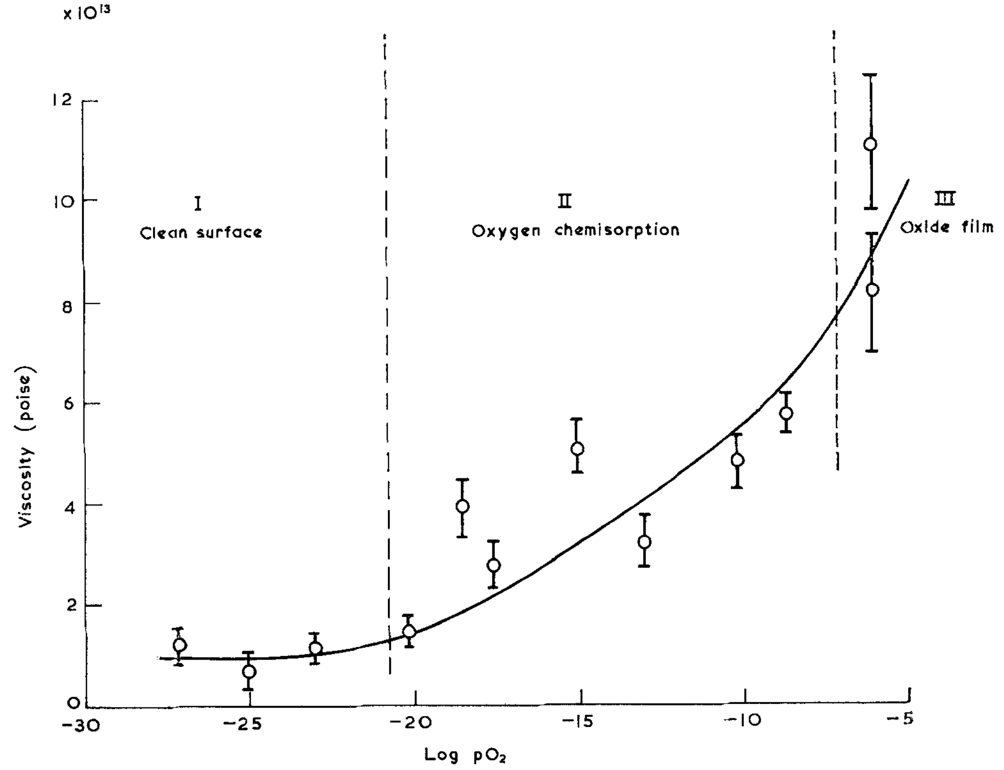

Figure 3 Viscosity of copper as a function of oxygen potential of the atmosphere.

interfaces not being efficient sources or sinks for vacancies.

3.3. Relevance to Sintering Kinetics

There is substantial evidence that the dominant material transport mechanism for the elimination of pores during high temperature sintering is viscous flow. The surfaces of the pores act as vacancy sources and nearby grain-boundaries behave as sinks: the diffusive flux of vacancies leads to the disappearance of the pores. Several authors have observed a strong inhibition of sintering rates in the presence of second phase dispersed particles, although there is no agreed explanation for this effect. In particular, Brett and Seigle [10] report this effect in copper containing dispersions of alumina and zirconia when heated in hydrogen. The effect was more marked at high temperatures. The present work may be relevant to these observations. Although the above metal oxides are considered normally very stable, the fact that some coarsening takes place indicates that there is some dissociation of the metal oxide. Thus at any instant, one might expect that the free oxygen in solution would correspond to the level of regime II, so that the pores contain a chemisorbed layer of oxygen, thereby inhibiting diffusion creep. The observation of these authors that pores develop facets in copper containing alumina supports this view; our recent measurements [7] show that for copper surfaces the anisotropy of surface energy is greatly enhanced in the presence of adsorbed oxygen, which should provoke facet formation.

Acknowledgement

This work forms part of the General Research Programme of the National Physical Laboratory.

References

1. L. ROTHERHAM, *Metals and Materials* **1** (1967) 15.
2. H. JONES, *Mater. Sci. Eng.* **4** (1969) 105.
3. E. D. HONDROS, *Phys. Stat. Sol.* **21** (1967) 375.
4. C. J. SMITHELLS, Metals Reference Book, 4th Ed., Vol. II (Butterworths, London, 1967) p. 644.
5. R. L. PASTOREK and R. A. RAPP, *Trans. AIME* **245** (1969) 1711.
6. A. B. LIDIARD, *Phil. Mag.* **5** (1960) 1171.
7. E. D. HONDROS and M. MCLEAN, Proceedings CNRS Conference, "La Structure et Les Propriétés des Surfaces Solides", Paris, 1969.

8. J. E. HARRIS and B. C. MASTERS, *Phil. Mag.* **13** (1966) 963.
9. J. E. HARRIS, R. B. JONES, G. W. GREENWOOD, and M. J. WARD, *J. Aust. Inst. Met.* **14** (1969) 154.
10. J. BRETT and L. SEIGLE, *Acta Met.* **14** (1966) 575.

Received 15 February and accepted 18 February 1970.