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The effect of phosphorus on creep in copper

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Abstract

Pure copper with an addition of about 50 ppm phosphorus is the planned material for the outer part of the waste package for spent nuclear fuel in Sweden. Phosphorus is added to improve the creep ductility but it also strongly increases the creep strength. In the present paper the influence of phosphorus on the strength properties of copper is analysed. Using the Labusch–Nabarro model it is demonstrated that 50 ppm has a negligible influence on the yield strength in accordance with observations. For slow moving dislocations, the interaction energy between the P-atoms and the dislocations gives rise to an agglomeration and a locking. The computed break away stresses are in agreement with the difference in creep stress of copper with and without P-additions.

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1. Background

It has been known for a long time that phosphorus enhances the creep strength of pure copper. Although their studies were limited to the initial stages of primary creep, Burghoff and Blank clearly demonstrated that the deoxidation of pure copper with 80 ppm P reduced the creep rates [1,2]. Again primary creep was the main interest of Kouta and Webster [3]. Their main finding was that both primary and secondary creep can be described by a single expression. The first who generated design data for P-deoxidised Cu based on long term creep tests were Drehfahl et al. [4]. They performed tests up to 20000 h. The P-content of their alloys was 200 ppm. They showed that P-deoxidised Cu has an adequate creep ductility and that the material is suitable for pressure vessels.

Andersson et al. studied the influence of phosphorus on the creep properties of oxygen free copper [5]. It was demonstrated that the creep strength and creep ductility were improved at 175 °C when 30 ppm P was added. No significant further improvement was observed when the P-content was raised more. The room temperature tensile properties were not noticeably influenced by the P-content. The phosphorus is in solid solution. Pure copper can dissolve up to 3.5 wt% P [6].

Hutchinson and Ray found that phosphorus, at least in larger concentrations, has a pronounced effect on both recovery and recrystallization [7]. They studied copper with 0.16 and 0.76 wt% P. When annealing 95% cold rolled sheet they observed that both processes could be retarded by more than a factor 1000. The influence on the recovery rate has a direct relevance for the creep behaviour since recovery of dislocations is often rate controlling. Hutchinson and Ray attributed the recovery retardation to the impurity locking of the dislocations. Further evidence for this conclusion was the fact that they observed strain ageing, which is in general believed to be caused by the locking of dislocations, see, e.g. [8]. It is the purpose of this paper

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to present models for the influence of P-solutes on the strength properties of copper.

2. Models for the influence of solutes

2.1. Labusch–Nabarro model

According to the Labusch–Nabarro model [9,10], the increase in the yield strength $\Delta R_{p0.2}$ is [11]

$$\Delta R_{p0.2} = K_{LN} \cdot \varepsilon_b^{4/3} \cdot c^{2/3}, \tag{1}$$

where K_{LN} is a constant. ε_b is the lattice misfit parameter which is 0.1651 for P in Cu [12]. c is the atomic fraction of the solutes. The model value for K_{LN} in MPa is

$$K_{LN} = 1.1 \times 10^{-3} \frac{m\alpha^{4/3} w^{1/3} G}{b^{1/3}}, \tag{2}$$

where m is the Taylor factor for fcc (3.06), $\alpha = 16$ is a constant. The interaction distance between solute and dislocation w is set to 2–5b, where b is Burgers vector and G the shear modulus. These assumptions give K_{LN} the value of 10400 MPa and $\Delta R_{p0.2} = 0.6$–0.8 MPa, which is a very small increase in the yield strength. This is also consistent with measured properties for pure copper with and without phosphorus. Handbook data gives no difference in tensile properties [13].

2.2. Solid solution during creep

The velocity v_{climb} of a climbing dislocation in a metal during creep can be expressed as [14]

$$v_{climb} = M_{climb} b \sigma_{app}, \tag{3}$$

where σ_{app} is the applied stress and M_{climb} the climb mobility

$$M_{climb} = \frac{D_s b}{kT}, \tag{4}$$

where D_s is the self diffusion coefficient, k is the Boltzmann constant and T the absolute temperature. The time t_0 for a dislocation to move one atomic distance is then given by

$$t_0 = \frac{b}{v_{climb}}. \tag{5}$$

Stresses from the solutes retard the dislocation. This can be taken into account by introducing the interaction energy E between the solute and the dislocation. In the elastic approximation the maximum value of E is given by [14]

$$E = -\frac{1}{2\pi} \frac{(1+\nu)}{(1-\nu)} G v_a \varepsilon_b, \tag{6}$$

where ν is Poisson's number and v_a the atomic volume. Inserting values for Cu gives -2.5×10^{-20} J at room temperature. The average time for the dislocation to pass a solute can be expressed as

$$t_{eff} = t_0 e^{\frac{|E|}{kT}}. \tag{7}$$

In addition the solute must diffuse away from the front of the dislocation. Using Einstein's equation the time t_{diff} can be expressed as

$$t_{diff} = \frac{b^2}{2D_P}, \tag{8}$$

where D_P is the diffusion coefficient for the P-solute in Cu. The total time for the dislocation to pass the solute is then $t_{tot} = t_{eff} + t_{diff}$. The relative increase in time t_{tot}/t_0 takes the form

$$\frac{t_{tot}}{t_0} = e^{\frac{|E|}{kT}} + \frac{b^3 D_s \sigma_{app}}{2D_P kT}. \tag{9}$$

Since $b^3\sigma_{app}/2kT < 1$ for Cu and $D_P \gg D_s$ for P in Cu, see Section 2.3, the second term is negligibly small. Eq. (9) gives $t_{tot}/t_0 = 179$, 93, and 56 at 75, 125 and 175 °C, respectively. If the corresponding analysis would be performed for glide instead, the only difference would be that the second term in Eq. (9) would disappear. Thus the result would be numerically identical since this term is negligible.

2.3. Solute drag

If solutes are attracted to the dislocations a Cottrell atmosphere might be formed, which creates a drag force. The interaction energy between a solute atom and an edge dislocation can be expressed as

$$W = -\frac{2bE}{3} \frac{y}{x^2 + y^2}, \tag{10}$$

where (x, y) is the position of the solute relative to a dislocation that is climbing in the y-direction or gliding in the x-direction, see Fig. 1.

The variation of the interaction energy according to Eq. (10) is illustrated in Fig. 2. For a climbing dislocation the solutes are repelled above the dislocation ($y > 0$) and attracted to the dislocation below ($y < 0$). For a gliding dislocation the P-solutes will primarily be positioned below the edge dislocation ($y < 0$), because the solutes are larger than the parent atoms and the interaction energy is

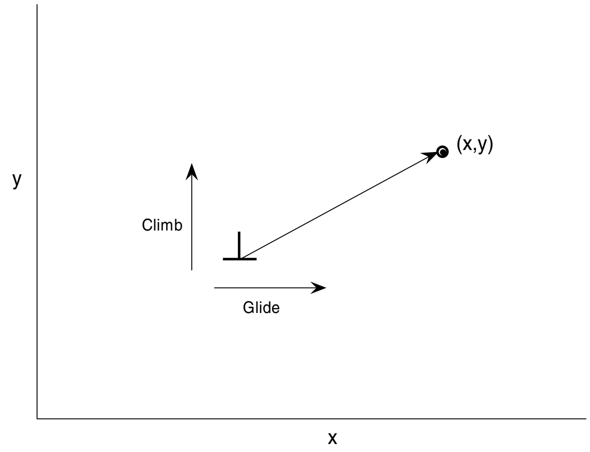

Fig. 1. Coordinate system for a climbing or gliding edge dislocation.