Embrittlement of Copper Due to Segregation of Oxygen to Grain Boundaries

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The tensile and creep properties of oxygen free OF- and oxygen saturated OS-polycrystalline copper have been investigated in the temperature range 25 to 500 °C. Oxygen increases the yield strength by a factor of 2 or 3, by solid solution hardening, and for coarse-grained copper, causes a severe embrittlement, particularly under creep conditions. Both direct and indirect evidence indicate that the embrittlement is caused by the segregation of oxygen to the grain boundaries in copper, thus promoting grain boundary decohesion and intergranular fracture. Auger electron spectroscopy is used to indicate the presence of oxygen at the grain boundaries in OS-Cu. The embrittling effects of oxygen are reversible in the sense that both tensile and creep ductility are restored when oxygen is removed.

Some metals and alloys can be severely embrittled by prior exposure to air or oxygen at elevated temperatures. This embrittlement is usually manifested by a dramatic reduction in rupture life associated with a loss of ductility. The mechanism of this embrittlement may involve the diffusion of oxygen to grain boundaries near the surface of the metal, which in turn leads to a reduction of the interfacial energy and grain boundary fracture strength.

The literature indicates that copper can be made brittle at room temperature by the presence of certain impurities; for example, both Sb and Bi have embrittling effects. This embrittlement is caused by the reduction of grain boundary cohesion associated with the segregation of solute atoms to the grain boundary. Tipler and McLean have shown that interfacial segregation of Sb in copper also occurs at high temperatures and leads to a reduction of the creep ductility. The presence of oxygen in copper also reduced the creep ductility and Tipler and McLean suggested that the embrittlement is due to grain boundary segregation of oxygen. Bleakney also found that the creep ductility of copper decreases with increasing oxygen partial pressure. Bleakney attributed the embrittlement effect to the intergranular absorption of oxygen. However, a systematic study of the mechanical properties of copper containing oxygen has not been conducted and direct evidence for oxygen segregation to grain boundaries in copper has not been given.

In this paper, both direct and indirect evidence is presented to indicate that oxygen segregates to grain boundaries in copper and causes an embrittlement, particularly under creep conditions. These embrittling effects of oxygen are reversible in the sense that ductility is restored when the oxygen is removed. The present study provides only a phenomenological description of oxygen embrittlement; the precise atomic mechanisms by which the embrittlement occurs have not been identified. Further, in this study, oxygen in copper caused a dramatic increase in the yield strength, due to solid solution hardening. This effect, although not directly related to the embrittlement is also documented and discussed.

EXPERIMENTAL

Certified-grade oxygen free-high conductivity (OFHC) copper was obtained, from American Brass and Copper Company, in plate form with a thickness of 3.2 mm. A spectrographic analysis of the material indicated 10 wt ppm Si, < 1 Mg, 8 Fe, 5 Ni, 20 Ag, 1 Ca and 3 Pb.

The as-received plates were cold-rolled to a thickness of 1.8 mm, from which both tensile and creep samples were machined. Unless otherwise specified, all samples were annealed at 950 °C for 3 h in a vacuum of 10^{-3} torr, which produced a stable grain size of about 1 mm. Throughout this paper we call this annealed material “OF-Cu” (OF stands for oxygen-free). Those specimens which were to be saturated with oxygen were additionally annealed in oxygen (P_{O_2} = 1 atm) at 800 °C for 2 h, and then water quenched. We refer to this material as “OS-Cu” (OS stands for oxygen-saturated). This annealing procedure is sufficient to allow oxygen diffusion to the center of the samples. Using the oxygen diffusivity, reported by Kirchheim, the diffusion depth X = \sqrt{4Dt} is 5 mm for a 2 h anneal at 800 °C. All specimens were mechanically polished prior to testing, to permit a more accurate determination of the cross-sectional area. But for OS-Cu, mechanical polishing is also required to remove the oxide scale from the surface.

All metallographic samples were prepared by mechanical polishing and etching with a solution of 2 g K_{2}Cr_{2}O_{7}, 4 ml HCl (saturated)-8 ml \text{H}_{2}\text{SO}_{4}, 100 ml H_{2}O. Both optical and scanning electron microscopy were used. The Auger analysis was done using a PHI Model 590 scanning Auger microprobe.
The high-temperature tensile tests were performed using a conventional Instron machine with an attached dual elliptical radiant furnace, as described elsewhere. Constant crosshead speed tensile tests were conducted at a nominal strain rate of $10^{-4}$ s$^{-1}$ over a wide range of temperatures (from 25 to 500 °C). Constant stress tension creep tests were conducted at 400 and 500 °C using an apparatus described elsewhere. To prevent oxidation, argon gas was used to provide an inert atmosphere during both the tensile and creep tests. We found the rupture behavior for tests conducted in argon and vacuum ($10^{-5}$ torr) to be essentially the same.

RESULTS

Room Temperature Hardness

Microhardness tests for OS-Cu at room temperature show that the hardness is quite uniform throughout the sample thickness and is much higher than that for OF-Cu. The Vickers hardness numbers are approximately 63 and 33 for OS- and OF-Cu, respectively. The stronger OS-Cu matrix is attributed to the dissolved oxygen in the copper lattice, as will be discussed later.

Tensile Properties of OF- and OS-Cu

Figure 1 shows the stress-strain curves for both OF- and OS-Cu at room temperatures ranging from 25 to 500 °C. The machine compliance is included in these plots. The low strain portions of some of the tensile curves in Fig. 1 are shown in Fig. 2 in expanded form. Because of the difficulty of resolving the yield stress of OF-Cu at the higher temperatures, only tensile curves at 25, 100 and 200 °C are shown. A comparison of the stress-strain curves indicates that OS-Cu invariably shows a higher yield stress than OF-Cu. This strengthening behavior is very significant and extends from room temperature to 500 °C.

Figure 3 shows how the 0.2 pct offset yield stresses vary with temperature for both OF- and OS-Cu. For OF-Cu, the yield stress variation with temperature is consistent with the data collected by Schmidt. The yield stress for OS-Cu is found to be two to three times higher than that for OF-Cu over the entire range of testing temperatures.

The comparison of stress-strain curves for OF- and OS-Cu shown in Fig. 1 also indicates that the tensile ductility for these two materials can be significantly different; the percentage elongation is plotted in Fig. 4. The OS-Cu material always exhibits a lower ductility than OF-Cu. At lower temperatures, e.g., room temperature, the ductilities are only slightly different. However, the difference becomes very significant as the temperature increases. For example, at 400 °C the percentage elongation for OS-Cu is only about 3 pct; for OF-Cu it is 18 pct.

The embrittling effect can be further demonstrated by examining the fracture surfaces of the two materials using scanning electron microscopy (SEM). For both OS- and OF-Cu, SEM shows a gradual change in the appearance of the fracture surface from a transgranular mode at low temperatures to an intergranular mode at high temperatures. For OS-Cu