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Role of Cu_2O during hot compression of 99.9% pure copper

V.G. García [a,*], J.M. Cabrera [a,b], J.M. Prado [a,b]

[a] CTM, Technological Centre, Av. Bases de Manresa 1, 08242 Manresa, Spain

[b] Department of Materials Science and Metallurgical Engineering, Universitat Politècnica de Catalunya, ETSEIB, Avda. Diagonal 647, 08028 Barcelona, Spain

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Abstract

Several authors have noticed that relatively pure coppers with different oxygen levels present a higher hot flow stress as the oxygen content increases. This work attempts to demonstrate that a large contribution to the observed increase of stress is due to precipitation of fine Cu_2O particles during hot working. Three fire-refined 99.9% pure coppers with different oxygen levels (26 ppm, 46 ppm, and 62 ppm) were hot compressed at temperatures 600–950 °C and at a strain rate range 0.001–0.3 s^{-1}. A comparison of transmission electron micrographs prepared from coppers compressed at 750 °C and 900 °C was performed to characterize the possible precipitates. Fine Cu_2O precipitates were found only in the two coppers with higher oxygen and at the lower temperature, where stress differences were larger. Precipitation–hardening theories were adapted for higher temperature and used to iteratively determine if the precipitate sizes and calculated volume fractions could be indeed causing an increase of stress.

Keywords: Copper; Dynamic precipitation; Hot compression

1. Introduction

The strengthening effect of dilute quantities of oxygen in copper had been reported on early works [1,2]. Fujiwara and Abiko [3] and Gao et al. [4] using high-purity coppers indirectly demonstrated that a higher oxygen content was responsible for a higher hot flow stress. A finer microstructure after dynamic recrystallization as oxygen content increased was also demonstrated [4]. However the latter works attributed the strengthening to solid atom interaction with dislocations.

Recently Prasad and Rao [5,6] based on measurements of the activation energy values obtained from hot flow curves (strain rates: 0.001–1 s^{-1}), have observed that the rate controlling mechanism changes from dislocation core diffusion to lattice self-diffusion at temperatures above 700 °C, as a consequence of the increased oxygen solubility at higher temperatures, in accordance to the Cu–O phase diagram [7,8]. Suggestions were made that an increase in interstitial oxygen clogs dislocation pipes, which essentially suppresses core diffusion. Solute strengthening was also suggested to occur due to non-symmetrical elastic distortions caused by interstitial oxygen; however no evidence of the distortions was shown. On the other hand Prasad and Rao [6] assert that the increase of apparent activation energy on coppers with increasing oxygen contents can be attributed to a back stress caused by the increase in the volume fraction of Cu_2O particles within the copper matrix. When oxygen amounts are much greater than the maximum solubility of Cu_2O in Cu, then the Cu_2O particles could be considered a dispersoid, because the volume fraction of Cu_2O is largely insoluble. The present study develops the latter precipitation–hardening hypothesis, by performing transmission electron micrographs of hot compressed 99.9% pure copper with three different oxygen amounts to characterize the possible precipitates.

The increase of hot flow stress as oxygen content increased was also noticed by the present authors [9,10], when three fire-refined coppers with 26 ppm, 46 ppm, and 62 ppm of oxygen were hot compressed at strain rates 0.001–0.3 s^{-1} and at a temperature range 600–950 °C. However the back stress, or increase in hot flow stress, was higher as temperature decreased particularly below 850 °C. This study pretends to demonstrate that precipitation during hot working, termed dynamic precipitation, occurs. The increase of stress was also correlated with the observed precipitate size and volume fraction using physically

* Corresponding author. Tel.: +34 93 877 7373; fax: +34 93 877 7374.
E-mail addresses: vgarcia@gmail.com (V.G. García), jose.maria.cabrera@upc.edu (J.M. Cabrera), jm.prado@upc.edu (J.M. Prado).

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established relationships for semicoherent and incoherent particles [11]. Additional evidence of precipitation–hardening is presented by measuring the Vickers hardness of the final hot compressed microstructure. The theoretical analysis shows the increase of hot flow stress can be described in terms of temperature, strain rate, volume fraction, and size of incoherent precipitates that nucleate, not only at grain boundaries, but within the copper matrix due to strain.

2. Experimental procedure

The three fire-refined and phosphorus de-oxidized coppers of this study were first cast into billets and then hot formed at ~950 °C, which is a temperature where relatively weak and comparable textures are expected. Residual oxygen content for the coppers named Cu A, Cu B and Cu C was 26 ppm, 46 ppm, and 62 ppm, respectively. Coppers were then machined into cylindrical test samples of 10-mm diameter and 15-mm height. Initial large-grained sizes of comparable hot flow behaviour [12] were obtained by previously annealing the Cu A and Cu B cylinders at 950 °C for 300 s, whereas Cu C cylinders required 900 s. The residual chemical composition and initial grain sizes are shown in Table 1. Hot compression tests were performed on the latter 99.9% pure coppers at a temperature range 600–950 °C and strain rates from 0.001 s^{-1} to 0.3 s^{-1}. Amounts of residual oxygen were found [9] to correlate well with the observed increase of flow stress at temperatures below 850 °C.

A TEM comparison was performed between samples compressed at higher temperature, where minimum stress differences were found and samples compressed at lower temperature, where considerable stress differences were noticed. A thin foil sample was prepared of each copper compressed at 950 °C and 750 °C and strained at 0.3 s^{-1}, which was the highest strain rate tested. A total of six samples were selected for jet electropolishing using a Struers Tenupol-3 machine. The electrolyte used was a solution of 80% methanol and 20% nitric acid. For corroboration purposes, the ion milling technique was also used to rule out the formation of fine crystals by a chemical reaction with the electrolyte. A Gatan dimple grinder model 656 was used to micromill a cavity using 9 μm diamond paste. Then to make the final thinning a Gatan precision ion polishing system model 691 was employed. Measurement of the room temperature mechanical properties would have been desirable, however the size of the compressed sample allowed few other tests than hardness tests.

Table 1
The residual chemical composition and the initial grain diameter, D_0, of the three fire-refined 99.9% pure coppers

ppm	P	Sn	Pb	Ni	Ag	S	Fe	Zn	O	D_0 (μm)
Cu A	297	86.2	63.5	31.7	30.8	22.0	17.2	15.6	26	637
Cu B	253	120	169	54.3	46.5	9.8	16.3	31.3	46	570
Cu C	153	63.3	133	40.0	37.7	10.1	15.5	13.4	62	530

Vickers hardness measurements were performed on the polished samples of the three coppers. The indentation load and time were 500 g and 30 s. On each compressed sample five measurements were taken, successive indentations followed a middle line perpendicular to the loading axis. The described indentation procedure minimized hardness reading variations, despite indenting on either the center or near the edge of the sample [13] or indenting on either one or many grains. The hardness value to be reported is the average of the five indentations performed on each sample.

3. Hot flow stress behaviour

The shape of the stress–strain curve was similar for coppers A, B, and C at equivalent temperature, T, and strain rate, $\dot{\varepsilon}$, conditions (i.e. equivalent Zener–Hollomon parameter values, $Z = \dot{\varepsilon}\exp(Q/RT)$ where Q is an activation energy and R is 8.314 kJ/K mol). However, the magnitude of flow stress at a given strain value was increasingly higher for the copper with higher oxygen content and that stress difference increased as the test temperature decreased. The σ–ε curves at 750 °C and 900 °C (Fig. 1) are an example of the explained behaviour, where Cu C with the highest oxygen content presented the highest stress values and Cu A with the lowest oxygen content presented with lowest stress values. Also in Fig. 1, stress differences between coppers are more noticeable at 750 °C than at 900 °C. A maximum peak stress, σ_p, which is a sign that dynamic recrystallization (DRX) has previously occurred [14], was observed on most of the conditions tested, with the exception of the highest Z conditions, however metallographic observations showed that DRX had begun on every condition tested [9].

The stress difference between coppers, or back stress σ_o, is also strain rate sensitive. As expected during hot working, the peak stress is higher as the strain rate increases; however, the magnitude of the back stress increases logarithmically with strain rate (note that σ_p vs. $\dot{\varepsilon}$ plots in Fig. 2 are curved not straight). The magnitude of the back stress, σ_o, on Cu B or Cu C can be estimated by subtracting the stress value of a pure copper,

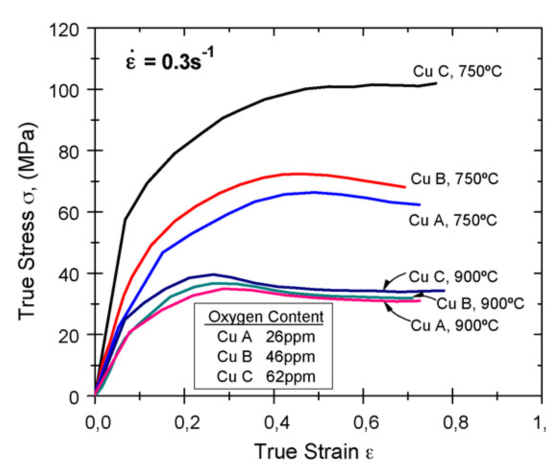

Fig. 1. Hot flow stress curves at 750 °C and 900 °C show that at the lower temperatures the flow stress differences are larger.