Materials Science & Engineering A 658 (2016) 393–399

Contents lists available at ScienceDirect

Materials Science & Engineering A

journal homepage: www.elsevier.com/locate/msea

Anneal hardening in cold rolled PM Cu-Au alloy

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ARTICLE INFO

Article history:
Received 13 November 2015
Received in revised form
8 February 2016
Accepted 9 February 2016
Available online 10 February 2016

Keywords:
Anneal hardening
Solute segregation
Short-range ordering
Hardening mechanism

ABSTRACT

Pure copper and Cu-11.4 wt%Au alloy were obtained by a powder metallurgy (PM) technique and subjected to thermomechanical treatment that was used to produce the conditions that led to an anneal hardening effect in the alloy. The results showed that low-temperature annealing of cold-rolled alloy caused a two-stage increase in hardness, microhardness and electrical conductivity. The mechanism of anneal hardening in this alloy was studied using differential thermal analysis (DTA), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The analysis of the DTA curve showed the presence of one endothermic and three exothermic reactions during the linear heating, which confirmed the occurrence of both short-range ordering and solute segregation. A decrease in the lattice parameter of the cold-rolled αCu-Au solid solution at the annealing temperature, which corresponded to the second hardness peak, was explained by solute clustering. Formation of precipitates in the copper-based matrix during annealing was not observed by TEM. It was confirmed that the dominant hardening mechanism during annealing was solute segregation towards lattice defects.

1. Introduction

It is well known that a softening process occurs in cold deformed metals and alloys during annealing as a result of recovery and recrystallization [1–5]. However, in the 1950s, a typical behaviour of some cold deformed copper alloys was found during annealing, i.e. during annealing, strengthening was found to occur up to the recrystallization temperature. The described phenomenon was termed “anneal hardening” by Nasiguti [6]. Since then, the anneal hardening effect has been found in several binary copper-based alloys with aluminium, gold, gallium, nickel, palladium, rhodium and zinc [7,8]. However, the origin of this phenomenon has not been fully explained. Some explanations have been offered by various research groups, among which two basic mechanisms are the most acceptable. The first mechanism involves the formation of ordered domains, which takes the decrease in the dislocation movement into account. Sugino et al. [9] introduced the concept of a partial long-range order of the Cu_3Al superlattice as an explanation of the anneal hardening phenomenon in Cu-Al alloys. Using XRD and microhardness and specific heat measurements, Kuwano et al. [10] showed that annealing influenced the recovery of short-range ordering in cold-worked Cu-14.2 at%Al alloys and growth of coherent domains. However, the second mechanism related to the interactions of solute atoms with lattice defects represents the dominant strengthening mechanism. Many authors have suggested that the combined effect of these mechanisms on properties change during the annealing of cold-deformed one-phase copper alloys. Popplewell and Crane [11] found that strengthening in Cu-Al alloys was associated with the development of ordered regions and Suzuki locking. Stacking faults had a very important role, representing the preferential nucleation sites for short-range ordering and chemical segregation of solute atoms. Bader et al. [8] cited the mutual interaction of the ordering effect and the solute segregation to lattice defects (vacancies, dislocations and stacking faults). They stated that the anneal hardening effect in Cu-16 at%Al alloys was predominantly related to the segregation of solute atoms to dislocations, but the formation of ordered clusters, especially at the dissociated dislocations, could not be excluded. Aruga et al. [12] studied low-temperature anneal hardening in very dilute Cu-Fe-P alloys with alloying concentrations of about 0.01%. They confirmed the decrease in dislocation density by a half and the increase in volume fraction of Fe-P clusters for a quadruple in surface regions.

According to the available literature, the anneal hardening effect has not been studied in Cu-Au alloys, except for the paper by

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http://dx.doi.org/10.1016/j.msea.2016.02.029
0921-5093/

Vitek and Warlimont [7]. Furthermore, no papers were found in the literature regarding the investigation of the anneal hardening effect in sintered copper-based alloys, except for the papers by the authors of this article [13–15]. Therefore, we studied the anneal hardening behaviour in sintered Cu-11.4 wt%Au alloy that had previously been cold-deformed by 60% reduction. This paper is an extension of a recent article [14] and further studies the intensity and mechanisms of the anneal hardening effect in sintered copper-gold alloys.

2. Experimental details

The Cu-11.4 wt%Au (Cu-11.4Au) alloy was prepared by a powder metallurgy (PM) technique using electrolytic copper powder (99.7% purity) and gold powder (99.93% purity) as starting materials. In order to compare the improvement in properties, pure copper samples were obtained and thermomechanically treated through the same route. The powders were mixed for 2 h using the Turbula T_2F triaxial mixer. Green (as-pressed) compacts were prepared using the Mohr-Federhaff-Losenhausen uniaxial hydraulic press at a pressure of 360 MPa. The prepared green compacts were cuboid in shape with an average length of 30.19 mm, width of 12.22 mm, and height of 6.32 mm. Subsequently, all the green compacts were sintered in the T-40/600 tube furnace at 850 °C for 1 h under a high-purity hydrogen atmosphere. The PM samples of pure copper and Cu-11.4Au alloy were pre-finally cold-rolled to the calculated height of 5 mm using the Marshall Richard rolling mill. The pre-finally rolled samples were annealed at 500 °C for 0.75 h under a hydrogen atmosphere and then quenched in ice water, producing a disordered α-solid solution in Cu-11.4Au alloy. Quenched samples were cold-rolled with 60% reduction using the Marshall Richard rolling mill, and isochronally and isothermally annealed using the Heraeus K-1150/2 electric resistance furnace. Isochronal annealing was carried out in the temperature range of 60–700 °C for a fixed duration of 0.5 h, followed by cooling in air. Isothermal annealing was carried out at 250 °C for up to 100 h.

Microhardness values were measured using a PMT-3 Vickers microhardness tester using 100 gf loads with a load duration of 15 s. Microhardness measurements were made on etched samples near to grain boundaries. Due to a strong dependence of microhardness values on load and a large scattering in microhardness results, hardness measurements were made to confirm the obtained results. Hardness values of the samples after annealing treatments were measured using a VEB Leipzig Vickers hardness tester using a 10 kg load and a 15 s dwelling time. The ASTM E384 standard was followed during both hardness and microhardness measurements. Electrical conductivity measuring was carried out using a Sigmatest 2.063 conductivity tester. All reported data were obtained from an average of at least 10 measurements. To study the mechanisms of the anneal hardening effect, differential thermal analysis (DTA), X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses were performed on cold-rolled Cu-11.4Au alloy with 60% reduction before and after annealing at 260 °C for 0.5 h. DTA analysis was performed using a TA Instruments SDT Q600 analyser with a constant heating rate of 5 °C min^{-1} under a flowing argon atmosphere. XRD analyses were performed using a Philips PW1710 diffractometer, operating at 40 kV/30 mA and using CuKα radiation (λ=0.154178 nm) in the 2θ range of 10–100°. For TEM analysis, discs were prepared by ion-beam thinning using a Gatan 691 PIPS ion polishing system. Thin electron-transparent discs were examined using a Jeol JEM 2010F transmission electron microscope at 200 kV operating voltage.

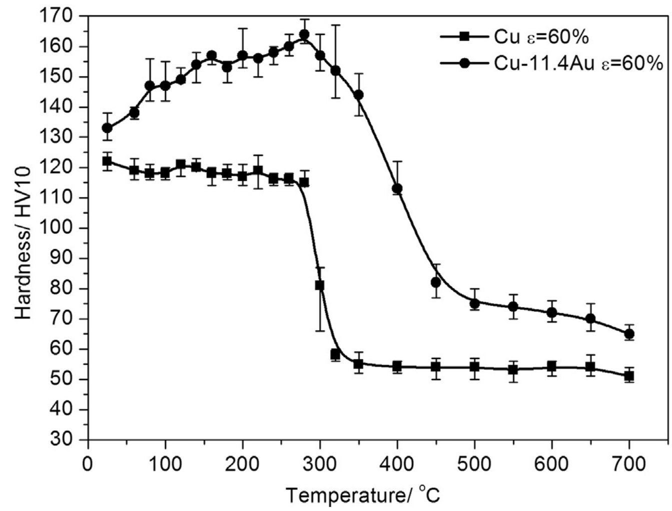

Fig. 1. Effect of annealing temperature on hardness values of cold-rolled copper and Cu-11.4Au alloy.

3. Results and discussion

3.1. Hardness

Fig. 1 shows the effect of annealing temperature on the hardness values of cold-rolled copper and Cu-11.4Au alloy samples with 60% reduction. The annealing curve for pure cold-rolled copper shows the typical behaviour of a cold-deformed metal, which is characterized by the existence of three stages: recovery, recrystallization, and grain growth [16,17]. In the recovery stage up to 280 °C, hardness is almost constant. A drastic decrease in hardness at 280–300 °C is due to recrystallization. In the grain-growth stage above 300 °C, the hardness continues to decrease, but much more slowly.

According to the hardness curve for cold-rolled Cu-11.4Au alloy, an atypical annealing behaviour of this solid solution is evident. An increase in hardness in cold-rolled Cu-11.4Au alloy was obtained during annealing at temperatures in the range 60–350 °C. This hardening is a result of the anneal hardening phenomena. The hardening process associated with annealing of cold-rolled Cu-11.4Au alloy can be divided into two stages, i.e. primary and secondary hardening. From room temperature to approximately 200 °C, primary hardening with a weak hardening effect occurred. The amount of primary hardening of cold-rolled Cu-11.4Au alloy with 60% reduction was about 24 HV10. The secondary hardening stage, which is when the main hardening effect occurred, was from 200 °C to 350 °C. The remarkable amount of secondary hardening of cold-rolled Cu-11.4Au alloy with 60% reduction was achieved for about 31 HV10 (from 133 HV10 to 164 HV10, after annealing at 280 °C). Above approximately 350 °C, a softening process occurs as a consequence of recrystallization. Rearrangement of grain boundaries during recrystallization results in a decrease in hardness and the formation of a recrystallized microstructure [18], as published elsewhere [14].

According to the literature [8], the primary hardening at lower temperatures is associated with the following processes: (a) migration and annihilation of interstitial atoms at dislocations and interstitial migration to solute atoms; (b) migration, clustering and annihilation of vacancies at dislocations. Vacancy migration increases the degree of short-range order in copper-based alloys, thus changing their properties [19,20]. The secondary hardening stage at higher temperatures is mainly attributed to the processes of segregation of solute atoms and their locking to lattice defects (vacancies, dislocations and stacking faults); however, the