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Modified strain rate regime in ultrafine grained copper with silver micro-alloying

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ABSTRACT

Ultrafine grained (UFG) copper with an average grain size of 115 nm was micro-alloyed with silver (UFG CuAg) to analyze its effect on strain rate sensitivity. The materials were prepared by sintering Ag microalloyed-Cu ultrafine powder, using the spark plasma sintering (SPS) technique and after H_2 pre-annealing for oxide reduction. Mechanical tests show that UFG CuAg follows the law of behavior established for UFG Cu: $m \approx B(1-\sigma_0/\sigma)$, relating the strain rate sensitivity m and the applied stress, σ. In this relation, σ_0 is a threshold grain size dependent stress and B is characterizing the grain boundaries diffusion properties. Main difference compared to pure UFG copper is a large value of the parameter B for UFG CuAg, indicating a dominant role of the grain boundaries structure and chemistry on the rheology of UFG metals.

1. Introduction

Improving the strength with preserving other properties like ductility and/or electrical conductivity, is a major issue for metallic materials [1]. Main strategies for strengthening consist in impeding dislocation formation and motion which naturally leads to stress localization in the weakest zones in the materials and eventually failure. Grain refinement is among these strategies; the strengthening is predicted by the Hall–Petch law and when entering the ultrafine grained domain, absence of plastic elongation is generally observed owing to absence of work-hardening [2]. However, there are few exceptions where ductility is preserved. A first example is low temperature bainite with Si addition. This alloy is formed of alternating nano-laths of ferrite and austenite where difference in phase properties and endogen nature of interfaces render the material likely resistant to localization [3]. A second example is the formation of multiple nano-twins structure [4]. In this particular case, coherent twin boundaries are able to resist to local softening with the build-up of local back stress inducing stress delocalization [5]. From these results the formation of complex microstructures or architectures is presumably the relevant solution for resisting to localization. Another complex example is the microstructure formed of thin 20 nm oriented Ni nanolaths separated by low angle grain boundaries revealing very high hardness [6]. Ductility is obtained owing to a coarse to nano grain sized gradient in the material. Under an applied stress, the materials undergoes simultaneously work-hardening and softening with gradual change in the mechanism between dislocations slip and grain boundary sliding [7].

In all cases, the nature of the grain and/or phase boundaries and in particular their properties regarding dislocations interactions seem dominant to obtain both strength and ductility [8,9]. This was captured experimentally by *in situ* transmission electron microscopy experiments [10]. It was emphasized by modeling based on the analysis of the thermally activated process in the deformation and also from numerical simulation [11]. For fine grained metals exhibiting general boundaries (no large fraction of twins, low angle or special grain boundaries), it is accepted that plastic deformation is dominated by diffusion controlled grain boundaries sliding [12]. Sliding is assisted by dislocations absorption that produces additional free volume in the boundaries facilitating atomic rearrangement [13]. It was emphasized that the atomic mobility in grain boundaries and then the grain boundary sliding is a function of the dislocations density, ρ.

It was first identified that this dependence has a detrimental effect on plasticity of the material. In absence of work hardening, elongation is due to a delay in necking in relation with large stain

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rate sensitivity m (Harts criterion). Then, its rapid decrease with increasing strain rate, $\dot{\epsilon}$, will lead to localization and rapid failure. In main works, strain rate applied in mechanical tests is of the order of $\epsilon \approx 10^{-3}\text{s}^{-1}$ and then absence of ductility in fine gained metals is systematically observed. Such behavior was described by the relation proposed in [5]. It indicates that elongation is expected in relation with sufficiently large value of m, at extremely low (or even unrealistic) stress and then strain rates. Meanwhile, the original model [8] predicts also, which was eventually proved [5] that above a reasonable strain rate, let say, $\epsilon > 10^{-3}\text{s}^{-1}$, a reverse effect occurs and the strain rate sensitivity increases with strain rate following, $m \approx B(1 - \sigma_0/\sigma)$. Where $\sigma_0 \approx Gb/d$, is the lower limit of the material strength depending of the grain size, d, the elastic modulus, G and the Burgers vector b. B is the higher limit of m at high stress, σ (or strain rate, $\dot{\epsilon}$). B is a dislocations density dependent grain boundary sliding parameter which can be defined as: $1/B \propto \partial D_{gb}/\partial\rho$, where D_{gb} is the grain boundary diffusion coefficient [14]. The relation shows that strain rate sensitivity should depend on the grain boundary properties and that m, should be as large as the boundary sliding is insensitive to dislocations.

The present paper reports on result to prove this assumption. Works are reported on the effect of the grain boundaries composition and diffusion properties, on the strain rate sensitivity of ultrafine grained copper (UFG Cu). Copper was alloyed with small amount (of the order of 0.1 atomic %) of silver (UFG CuAg). Such low alloying giving diluted solid solution, is known for having no effect on the copper properties, except on those related to grain boundaries. Strength and deformation properties are nearly unchanged[2] but thermal stability is improved with increase in temperatures of recovery and grain coarsening [15]. Solubility of Ag in copper is very low and works reported in the literature were mainly conducted on the effect of Ag precipitation in UFG copper [16]. Here, very low alloying effect on rheology is investigated for designing UFG copper with more appropriate rheology regarding potential applications in particular for electric devices.

2. Experimental

UFG CuAg alloys were prepared using powder metallurgy techniques [17]. Ultrafine powder was produced by evaporation from an electromagnetic overheated metal droplet of copper, starting with 0.4 atomic % of silver and condensation of the vapor produced in liquid nitrogen. The technique called cryo-condensation is detailed in [18,19]. Composition of the starting material was identified after an analysis of the evaporation from various $Cu_{(1-x)}Ag_x$ alloys with $x < 0.003$ atomic [20]. Solubility of Ag in Cu at room temperature is lower than 0.15 at% [21]. However, as the vapor is condensed in a cryogenic medium with an extremely high solidification rate, supersaturated solid solution of alloys in ultrafine particles is generally obtained. In addition, as Ag has larger vapor tension than Cu, gradual deviation in composition is observed during the particles formation owing to impoverishing in Ag of the liquid droplet source. The particles are produced with an average 0.7 at% of silver at the beginning of the experiment and can have less that 0.1 at% of silver at the end depending on the experiment duration. For the study of silver effect on the rheology of ultrafine grained copper, the powders must contain at least 0.1 at% of silver to be sure that the grain boundaries are close to saturation.

In the formation procedure of the bulk material, ultrafine powders were first compacted in steel die and punch tools into the form of 3 mm thick and 30 mm diameter pellet. The green specimen with a relative density of 70% were then annealed under H_2 gas flow at 400 °C to reduce metallic oxides present at the particle surface. Then the sintering to consolidate and complete densification of the material was carried out using the spark plasma sintering technique (SPS Dr Sinter 515S Syntex). Similar procedure was applied and analyzed in details for pure ultrafine copper powder [22]. In particular the SPS processing was proved efficient to produce dense ultrafine metal with limiting grain coarsening. Dog bone specimens were cut off from the pellets for mechanical tensile tests carried out with a MTS 20 machine at room temperature. Alloys were characterized using transmission electron microscopy (TEM Technai FEI F20 microscope with FEG, TEM, STEM, HAADF imaging mode and ACOM ASTAR orientation mapping technique). Scanning Transmission Electron Microscopy (STEM) observations were carried out on a JEOL ARM-200F probe corrected microscope operating at 200 kV with a probe size of 0.2 nm and a convergence angle of 34 mrad. High Angle Annular Dark Field (HAADF) images were recorded with a collection angle ranging from 50 to 180 mrad and Dark Field (DF) images with a collection angle ranging from 20 to 50 mrad.TEM specimens were prepared by mechanical thinning and finishing by electropolishing in a tenupol with D2 Struers solution. CuAg solid solution was analyzed with atom probe tomography technique (APT). The samples were prepared by standard electropolishing techniques [23]. Analyses were performed in ultra high vacuum conditions, using an energy compensated atom probe equipped with an ADLD detector [24] and a reflectron. Samples were field evaporated at 30 K using electric pulses (30 kHz pulse repetition rate and 20% pulse fraction). Facture surface were observed with a field emission gun Zeiss MERLIN scanning electron microscope.

3. Microstructure and composition of the alloy

Atom probe tomography shows that silver is homogenously distributed in copper, forming a solid solution with a composition of about 0.119 ± 0.004 at%Ag (Fig. 1). This result is consistent with Cu–Ag phase diagram [21]. Due to limitations in spatial resolution

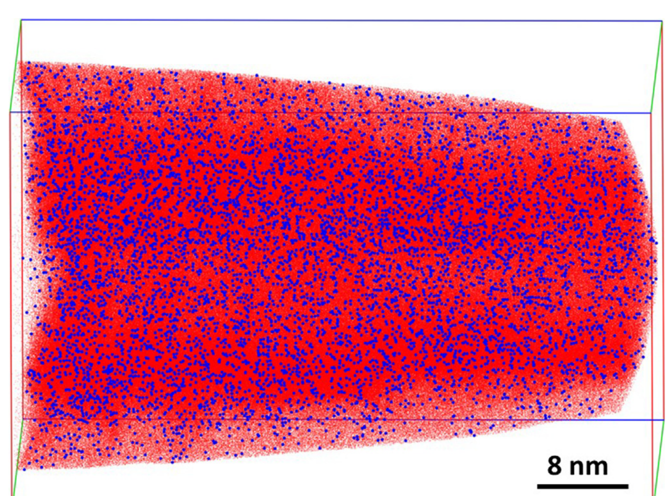

Fig. 1. 3D atom probe tomography image showing the distribution of Ag in ultrafine Cu grain.

[2] According to Lambush (R. Lambush, Phys. Stat. Sol. 41 (1970) 659) contribution of solid solution to alloy strengthening is given by $\sigma_{ss} = 3 \times (\frac{G}{550})\varepsilon_L^{4/3}c^{2/3}$. G=41 GPa is the shear modulus of copper, ε_L is a parameter including atomic size misfit and solute-solvent shear modulus, evaluated of the order of 4 using data from (R.L. Fleischer, Acta Met 11 (1963) 203), c is the silver content with a maximum value of 0.12%. Then the Lambush equation estimates that the maximum contribution is about $\sigma_{ss} \approx 2$ MPa which is not more than 0.5% of UFG Cu strength.