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Thermal stability of electrical and mechanical properties of cryo-drawn Cu and CuZr wires

A. Kauffmann [a,b], D. Geissler [a], J. Freudenberger [a,*]

[a] IFW Dresden, P.O. Box 270116, 01171 Dresden, Germany

[b] Institute for Applied Materials (IAM-WK), Karlsruhe Institute of Technology (KIT), Engelbert-Arnold-Straße 4, D-76131 Karlsruhe, Germany

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ABSTRACT

Low temperature deformation results in a considerable refinement of the microstructure of polycrystalline copper by extensive deformation twinning in the case of cryogenic wire drawing. In order to improve the thermal stability of the obtained microstructure, we investigate the deformation of CuZr alloys with up to 0.21 at% (0.3 wt%) Zr by drawing in liquid nitrogen up to a true strain of 2.4. An ultimate tensile strength of 625 MPa in combination with an electrical conductivity of about 60%IACS was found for an initially solution annealed CuZr0.21 alloy. For an initially precipitation treated CuZr0.21, a slightly lower ultimate tensile strength of 600 MPa at about 86%IACS was observed in the as-deformed state. Deformation twinning could be identified in all investigated materials, leading to a refinement of the microstructure. Thermal stability of microstructure as well as electrical and mechanical properties can be significantly improved by the addition of Zr. For cryo-drawn copper the drop of hardness due to recovery and recrystallization occurs between 200 °C and 225 °C for an annealing duration of 30 min. Small recrystallized grains are already identified at 175 °C. In CuZr0.21, a stable microstructure is found up to 350 °C for the solution annealed material while small recrystallized grains are found already at 300 °C in the precipitation treated material. By annealing a homogenized and subsequently cryo-drawn CuZr0.21 at 350 °C for 30 min, ultimate tensile strength can be further increased up to 635 MPa while electrical conductivity is enhanced significantly to 70%IACS by partial precipitation of Cu_5Zr. Dynamic resistivity measurements indicate that this heat treatment subsequent to cryo-drawing does not affect the thermal stability of the prepared material.

1. Introduction

Low temperature deformation enables a considerable refinement of the microstructure of polycrystalline copper by extensive deformation twinning as it has been shown for wire drawing by immersion into liquid nitrogen previously [1,2]. Similar to electro-plated films [3], the refinement by twinning results in a significant increase of mechanical strength when compared to non-twinned counterparts [2,4]. Nevertheless, the strength increase in cryo-drawn material is less pronounced in comparison to electro-deposited thin films [3,5]. Additionally, a rather high dislocation density which is amplified by suppressed dynamic recovery during cryo-drawing of Cu limits its thermal stability. Subsequent to cryo-drawing up to a true strain of 2.4, dynamic resistivity measurements at a constant heating rate of 0.5 K/min revealed an onset of recovery and recrystallization at about 175 °C and completion of recrystallization at 250 °C, respectively [2].

Similarly, Cu subjected to cryo-rolling, where deformation twinning plays a minor role for grain refinement [6], lacks significant thermal stability. Konkova et al. [7] found recrystallization to be finished within 8 min at 150 °C after a rolling reduction of 90%. Even at room temperature long-term storage leads to significant changes of the microstructure by recovery and early stages of recrystallization [8]. Thus, in order to take technical advantage of the enhanced mechanical strength of the materials after cryogenic deformation, reasonable improvements regarding thermal stability have to be found.

A well-established possibility for improving thermal stability of Cu alloys while keeping a high level of electrical conductivity is alloying with Zr [9]. Zr exhibits a maximum solubility of about 0.1 at% in Cu at about 980 °C [10]. A pronounced decreasing solubility of Zr at lower temperature enables the precipitation of Cu_5Zr (based on the crystallographic prototype of the phase, namely $AuBe_5$; deviating stiochiometry is possible, please see [10]). Precipitation hardened CuZr alloys are characterized by a comparably high electrical conductivity well above 80%IACS depending on the

* Corresponding author.
E-mail address: j.freudenberger@ifw-dresden.de (J. Freudenberger).

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solute concentration in combination with a softening temperature of maximum 600 °C [9]. As an (electrical) engineering material, CuZr0.07 (0.1 m% Zr) is standardized as CW120C in DIN CEN/TS 13388.

In the present study, the influence of Zr addition in the form of solute atoms as well as Cu_5Zr precipitates on the recrystallization of cryo-drawn Cu is investigated. Their impact on the ability for twin formation during cryo-deformation as well as the resulting mechanical strength, electrical conductivity and thermal stability are presented.

2. Experimental

Three CuZr alloys with nominal composition of 0.1, 0.2 and 0.3 m% were prepared by induction melting and cast into a graphite mold under argon atmosphere. This corresponds to atomic fractions of 0.07, 0.14 and 0.21 at%, respectively. Hence, the alloys are named with CuZr0.07, CuZr0.14 as well as CuZr0.21 throughout the article. The purity of the starting materials was 99.99 % and above. Zr addition was realized by adding a CuZr30 master alloy into the Cu melt. The alloys were homogenized at 950 °C for 6 h in argon atmosphere and subsequently water-quenched. Surface near cast defects were removed by machining to a diameter of 26 mm. In order to prepare a suitable initial microstructure, room temperature rotary swaging down to a diameter of 10.4 mm and subsequent heat treatment were applied. Two types of initial microstructures were prepared. The first type was annealed for 1 h at 700 °C to ensure complete recrystallization of the three alloys. A mean grain size decreasing from 30 to 10 μm was observed with increasing solute concentration. Therefore, a comparison with the study of pure Cu in Ref. [2] is possible. In addition to recrystallization, precipitation of Cu_5Zr occurs in form of spherical particles of about 70–90 nm in diameter. Throughout the article these recrystallized and precipitation treated alloys are highlighted by “prec.”. The second type of microstructure was prepared by solution annealing at 950 °C for 6 h under argon atmosphere and subsequent water quenching. In CuZr0.14 as well as CuZr0.21, Cu_5Zr from the solidification process were found as coarsened particles of about 1–5 μm which cannot be removed by the solution annealing. In contrast, CuZr0.07 is single-phase after solution annealing. Due to the high temperature homogenization, the starting grain size for the following study is found to be in the submillimeter range. Throughout the article, these solution annealed alloys are highlighted by “homog.”. All types of alloys were subjected to cryo-drawing in the same manner as described in Ref. [2]. Samples from cryo-drawing and drawing at room temperature are highlighted by “CT” and “RT”, respectively.

Microstructural characterization was carried out by scanning electron microscopy (SEM) using a FEI Helios 600i operating at 20 kV and 11 nA. Electron backscatter diffraction (EBSD) was performed using an EDAX DigiView system. Microhardness measurements were performed on a Shimadzu HMV-2 hardness tester operating at a load of 0.98 N. The samples were prepared by a conventional metallographic procedure. Finally, vibratory polishing (VibroMet® 2) with Mastermet® 2 suspension (both by Buehler) was applied for optimal surface finishing for about 8 h. Tensile tests were performed at room temperature on as-drawn samples with a total length of 140 mm using an electromechanical Instron 8562 testing machine at a cross head displacement rate of 0.1 mm/min. Dynamic resistivity measurements were performed at a heating rate of 0.5 K/min using the four-probe technique as described elsewhere [11]. For reference, a well annealed state was investigated after heating to 750 °C with 0.5 K/min, a dwell time of 1 h and cooling with approximately 0.5 K/min which corresponds to a complete experiment using the described resistivity setup.

3. Results and discussion

3.1. Mechanical properties of the as-deformed materials

Fig. 1 shows the ultimate tensile strength of Cu and CuZr alloys subjected to wire-drawing in liquid nitrogen (“CT”) in comparison to Cu drawn without cooling (“RT”) (from Ref. [2]). Low temperature deformation by liquid nitrogen cooling results in an increase of strength of about 35% due to deformation twinning and the suppression of dynamic recovery [2]. The addition of Zr provides a hardening of less than 50 MPa in the precipitation treated and deformed as well as the homogenized and deformed state. The hardening of the homogenized and subsequently deformed alloys is slightly more pronounced. This is on the one hand attributed to the negligible hardening due to Cu_5Zr precipitates because of the coarse size of the precipitates after precipitation at 700 °C. At a particle size of about 70 nm to 90 nm no significant hardening is expected. On the other hand, the homogenized and deformed material exhibits a solid solution hardening. The deformation process does not lead to any alignment or shape change of the initially spherical particles. Nonetheless, complete precipitation leads to a considerable benefit regarding electrical resistivity as it will be shown later. Experiments concerning the room temperature deformation of precipitation or solution treated material were not performed since a similar dependence of the mechanical properties is to be expected with the exception of the hardening contribution by deformation twinning and suppressed dynamic recovery as in the case of the cryo-deformed material. This will be discussed in more detail in the following paragraphs.

3.2. Microstructure of the as-deformed materials

Fig. 2 shows orientation mappings of CuZr0.07 and CuZr0.21 following cryo-drawing of the precipitation treated and solution annealed state in comparison to the observations on pure deformed Cu. It can be seen that twinning is activated in all alloys during cryo-drawing (twins/twin bands are indicated by white arrows). In the case of the homogenized alloys the initial solution annealing results in coarsened matrix grains when compared to the precipitation treated samples. Non-indexed regions of the mappings on CuZr0.21 in Fig. 2e and f are caused by coarse Cu_5Zr particles arising from the solidification due to surpassing the maximum solubility of Zr in Cu. Deformation evolves inhomogeneously at these particles but formability does not seem to be affected at all.

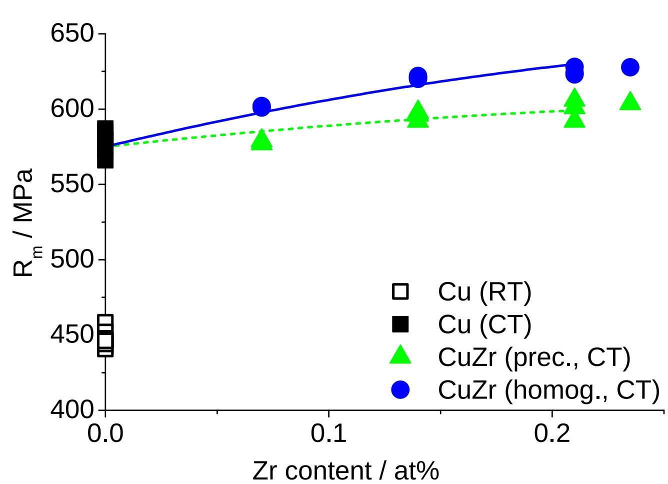

Fig. 1. Ultimate tensile strength of Cu and CuZr alloys subjected to cryo-drawing up to a true strain of 2.4 in comparison to Cu drawn without cooling. Experiments on pure Cu according to Ref. [2].