Materials Science & Engineering A 649 (2016) 209–213

Contents lists available at ScienceDirect

Materials Science & Engineering A

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

Short communication

High strength–high conductivity nanostructured copper wires prepared by spark plasma sintering and room-temperature severe plastic deformation

Claire Arnaud [a,b], Florence Lecouturier [b], David Mesguich [a], Nelson Ferreira [b], Geoffroy Chevallier [a,c], Claude Estournès [a,c], Alicia Weibel [a], Alain Peigney [a], Christophe Laurent [a,*]

[a] Université de Toulouse, Institut Carnot CIRIMAT, UMR CNRS-UPS-INP 5085, Université Paul-Sabatier, 118 Route de Narbonne, F-31062 Toulouse Cedex 9, France
[b] Laboratoire National des Champs Magnétiques Intenses, UPR CNRS-UPS-INSA-UJF 3228, 143 Avenue de Rangueil, F-31400 Toulouse, France
[c] Plateforme Nationale CNRS de Frittage Flash, PNF2 MHT, Université Paul-Sabatier, 118 Route de Narbonne, F-31062 Toulouse Cedex 9, France

ARTICLE INFO

Article history:
Received 15 April 2015
Received in revised form
17 September 2015
Accepted 30 September 2015
Available online 3 October 2015

Keywords:
Copper
Spark plasma sintering
Wire-drawing
Nanostructured materials
Mechanical strength
Electrical resistivity

ABSTRACT

A pure copper cylinder with micrometric grains was prepared by spark plasma sintering and was wire-drawn at room temperature. The ultimate tensile strength of the conducting wires is 600 MPa at room temperature. This originates from the propagation of dislocations by an Orowan mechanism in grains smaller than 250 nm.

1. Introduction

There is a demand for stronger yet lighter conducting copper wires, in global fields where weight is at a premium such as aeronautics, space and power transportation as well as in niche applications such as materials for high-field magnets. However, high mechanical strength and high electrical conductivity seem to be mutually exclusive properties of metals. In polycrystalline, 'engineering' metals, the strength is limited by the onset of plastic deformation, which is mainly carried by lattice dislocations within the crystalline grains. To strengthen a metal, this dislocation motion has to be reduced. This can be achieved by alloying, by introducing another phase or by introducing extra grain boundaries through grain refinement. Strengthening by nanostructuring [1–8] is highly attractive as compared to alloying, because it requires little extra energy and allows for easy recycling of the metal. In general, all these strengthening methods also increase scattering of the conducting electrons, i.e. they decrease the electrical conductivity. This impasse was broken when it was shown that a specific type of grain boundary, the coherent twin boundary, can strengthen electrochemically deposited copper films without introducing additional electron scattering, resulting in high strength-high conductivity thin films [9–11]. Similar results were achieved with nanotwinned bulk materials prepared using cryo-deformation [12–14]. However, a considerably altered electrical conductivity suggested the formation of non-coherent twin boundaries or destructed twin orientation relationship in these cryo-drawn wires [14]. Interestingly, these authors observed that a coarse-grained initial microstructure yields a slightly lower mechanical strength for wires drawn at room temperature while the ultimate tensile strength of cryo-drawn copper is not altered by the initial microstructure. Indeed, the tensile strength of a Cu wire deep-drawn at room temperature from an initial Cu cylinder with a mean grain size of 9.4 μm reached 460 MPa [15] and is usually below 400 MPa [1]. Therefore, it was hypothesized for the present work that, in order to produce high-strength wires by room-temperature wire-drawing, it is a necessity to start from a precursor cylinder with grains one order of magnitude smaller, i.e. micrometer-sized, than conventional cylinders. The modest degree of grain refinement thus endured would not introduce much

* Corresponding author.
E-mail address: laurent@chimie.ups-tlse.fr (C. Laurent).

http://dx.doi.org/10.1016/j.msea.2015.09.122
0921-5093/

additional scattering, maintaining a high electrical conductivity. However, producing such a micrometer-sized Cu precursor cylinder is not straightforward because of the rapid increase in grain size upon exposition to the elevated temperatures necessary for sintering a Cu powder. To circumvent this, we propose to prepare the precursor cylinder with spark plasma sintering (SPS), the application of a pulsed direct current to a pressed powder [16,17]. The advantages of SPS over other sintering methods include lower sintering temperatures and shorter sintering times, which can produce Cu pellets with limited grain growth [18–20]. Cu wires then produced by room-temperature wire-drawing show an electrical conductivity of more than 84% International Annealed Copper Standard (IACS), at room temperature with an ultimate tensile strength (UTS) of 600 MPa, 50% higher than when using standard precursor cylinders.

2. Experimental procedures

A Cu cylinder was prepared by SPS (see supporting information). It was cold-drawn at room temperature. Samples of wires were typically 70 cm or 150 cm long. The total true strain (η) reached 7.29 with η given by $\eta = \ln(A_0/A)$ where A_0 is the cross-sectional area of the cylinder and A is the cross-sectional area of the wire. For the sake of comparison, wires were also prepared by the same route using a conventional cylinder (average grain size of the order of 10 μm) prepared from standard cast oxygen-free high conductivity (OFHC) Cu.

Analysis of the X-ray diffraction (XRD) patterns (see supporting information) revealed only traces of Cu_2O for the powder while no copper oxide is detected after SPS (Fig. S1), reflecting that the SPS experimental conditions are reducing. It is known [21] that for Cu nanopowders, the initial presence of CuO will favor the formation of Cu_2O during SPS due to the anti-dismutation reaction $Cu + CuO \rightarrow Cu_2O$, but it is not the case here.

The relative density of the cylinder and wires was measured by Archimedes' method. The cylinder and transversal and longitudinal sections of selected wires were observed by scanning electron microscopy (SEM, JEOL JSM 6700 F) and transmission electron microscopy (TEM, JEOL JEM 2100 F operated at 120 kV). The electrical resistivity was measured at 293 K and 77 K for wires W5-W12 using the four probe method with a maximum current of 100 mA to avoid heating the wires. Microhardness was determined from indentation tests (1 N for 10 s in air at room temperature) performed on the polished transverse surface of wires by loading with a Vickers indenter (Shimadzu HMV M3). Tensile tests (INSTRON 1195 machine) were performed at 293 K and 77 K on 170 mm long specimens. The tensile direction was parallel to the wire-drawing direction. During the tests, precise stresses were measured by the stress gauge system (250 N), under displacement control at a speed rate of 1.6×10^{-5} m s^{-1}. The denser wires were tested.

3. Results and discussion

3.1. Density and microstructure of the cylinder and wires

The relative density for the cylinder is equal to 86 ± 1%. While not high, this value was found convenient for the rest of the study, in particular because a too high density hampers the deformability of the cylinder during wire-drawing, resulting in sample breaking. TEM observations (Fig. 1) of a transversal section of the cylinder reveal that the Cu grains have not grown significantly from the original size (1.0 ± 0.5 μm) and contain twins *ca.* 100 nm thick (arrowed in Fig. 1) with a spacing about 300 nm. Zhang et al. [22] observed the presence of extensive nanoscale twins with different spacing (about 60 nm and less than 2 nm) in bulk Cu prepared by SPS in different conditions than the present ones (300 °C, 600 MPa). They observed that the average nanoscale twin width increases upon the increase of the sintering temperature. Thus, the twins observed in the present sample could correspond to their larger-spacing twins whereas no twins with very small spacing are observed because we use a much lower SPS uniaxial pressure (25 *vs* 600 MPa).

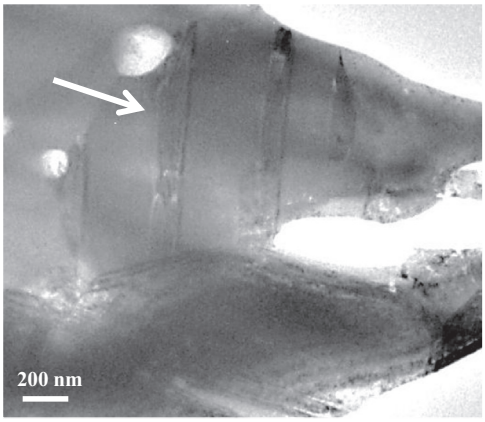

Fig. 1. TEM bright-field image of the transversal section of the Cu cylinder (8 mm in diameter) prepared by SPS showing a micrometric grain containing twins (arrowed).

Twelve wires (designated W1-W12 hereafter) were selected for the study (Table 1). For example, the diameter of W8 and W12 is equal to 0.506 and 0.198 mm, respectively and η is equal to 5.41 and 7.29, respectively, corresponding to very large strains [23]. The relative density is significantly higher for W1 (94 ± 1%) than for the cylinder (86 ± 1%) and increases up to 97 ± 3% for W8. It is probably still higher for W9–W12 but the measurement uncertainty is too high to give a meaningful value. The fact that the wires did not break during the wire-drawing (WD) process reveals that the residual porosity in the cylinder allows for grain rotation in the beginning of the drawing process (see XRD section in supporting information) and, once a higher density is achieved, for grain deformation.

Transverse SEM (Fig. 2a) and TEM observations (Fig. 2c) of W8 reveal 50–400 nm grains, three quarter of them smaller than 260 nm (Fig. 2b). TEM observations of a longitudinal section of W8 (Fig. 3), i.e. parallel to the WD direction, show the so-called lamellar microstructure [23]. Grains are dramatically elongated over

Table 1
Diameter, electrical resistivity and microhardness of the cylinder and wires. Sample, diameter, the corresponding total true strain η, electrical resistivity at 293 K ($\rho_{293\ K}$) and 77 K ($\rho_{77\ K}$), Vickers microhardness (Hv).

Sample	Diameter (mm)	η	$\rho_{293\ K}$ (10^{-8} Ω m)	$\rho_{77\ K}$ (10^{-8} Ω m)	Hv (GPa)
Cylinder	7.560	0.00	–	–	0.58
W1	3.300	1.66	–	–	1.21
W2	2.064	2.60	–	–	1.23
W3	1.511	3.23	–	–	1.26
W4	0.809	4.47	–	–	1.33
W5	0.640	4.94	2.07	0.48	1.43
W6	0.592	5.10	2.01	0.47	1.44
W7	0.547	5.26	2.05	0.48	1.45
W8	0.506	5.41	2.05	0.48	1.48
W9	0.401	5.88	2.08	0.49	1.39
W10	0.293	6.51	2.19	0.52	1.52
W11	0.251	6.82	2.16	0.52	1.54
W12	0.198	7.29	2.24	0.55	1.61