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Correlation between the nanomechanical properties and microstructure of ultrafine-grained copper produced by equal channel angular pressing

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Abstract

Ultrafine-grained copper was manufactured by equal channel angular pressing technique. Microstructural observations performed with the aid of transmission electron microscopy and scanning force microscopy revealed that short annealings of as-pressed material in the temperature range 250–300 °C result in a duplex microstructure consisting of micrometer-sized and relatively defect-free recrystallized grains embedded in the untransformed ultrafine-grained matrix. It was found that the nanohardness of newly nucleated grains in partly recrystallized samples is very different from the nanohardness of untransformed matrix, the latter being identical with the nanohardness of as-pressed samples. Extensive pile-ups around the indents were observed in the as-pressed samples, while the pile-ups were virtually non-existent in the sample annealed at high temperature. In as-pressed samples the pile-ups relaxed with time at room temperature. Grain boundary sliding was suggested as a possible mechanism of this relaxation.

Keywords: Equal channel angular pressing; Scanning force microscopy; Nanoindentation; Hardness

1. Introduction

Mechanical and functional properties of ultrafine-grained and nanocrystalline metallic materials have become the subject of intensive studies over the past decade [1]. It was shown that the classical method of increasing yield stress and strength of polycrystalline materials by decreasing grain size reliably works down to the grain sizes of few dozens of nanometers. Unusual functional properties of nanocrystalline materials are attributed to the large fraction of the total number of atoms that are located inside distorted environment of grain boundaries (GBs) and other crystalline defects [2]. A wide variety of methods for manufacturing of ultrafine-grained and nanocrystalline materials are currently available: consolidation of nanopowders, electrodeposition, crystallization of amorphous alloys, and severe plastic deformation (SPD). Among them, the equal channel angular pressing (ECAP) technique that belongs to the family of SPD methods offers several important advantages over its competitors: bulk quantities of ultrafine grain material can be produced at relatively low costs and in short times; the technique is suitable both for pure metals and for alloys; no foreign impurities are introduced during processing and the samples are free from residual porosity [3]. However, the high strength of ultrafine grain materials manufactured by SPD methods is often accompanied by their poor ductility [4]. It was recently shown that short annealings of as-processed nanocrystalline Cu that produce a duplex microstructure consisting of relatively large recrystallized grains embedded into nanocrystalline matrix can significantly improve the ductility of Cu without compromising its strength [5]. It was suggested [5] that remaining nanocrystalline matrix is responsible for the high strength, while the large recrystallized grains contribute to plasticity. Though this is a plausible hypothesis, direct experimental measurements of

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mechanical properties of the individual elements of duplex microstructure were never performed so far. Though it is well known that heavily deformed metals fully recover their high ductility and relatively low strength after recrystallization, the mechanical properties of a newly nucleated individual submicrometer-sized grain embedded in the nanocrystalline matrix may be different from those of its larger counterparts in the fully recrystallized material. At the same time, the nanocrystalline matrix may lose part of its strength after annealing even without significant grain growth. This is related to the recovery processes that precede recrystallization [6]. Therefore, the knowledge of the in-situ mechanical properties of the individual elements of microstructure is needed for understanding of macroscopic mechanical behavior of the materials with duplex microstructure, such as those produced by Wang et al. by annealing of SPD-processed Cu [5].

In this study, we employed the Hysitron Triboscope (Hysitron Inc., Minneapolis MN, USA) attachment to the scanning force microscope (SFM) for studying the mechanical properties of the individual components of the microstructure in partly recrystallized ultrafine-grained Cu. The Triboscope allows imaging of the sample surface prior to indentation in the SFM mode using the same diamond tip that is later employed for depth-sensing nanoindentation. With the appropriate surface preparation that makes different elements of microstructure visible in the SFM, spatially-resolved measurements of their mechanical properties become possible. This method has been employed by Göken et al. in their studies of multiphase metallic alloys [7–9]. However, to our knowledge no nanoindentation measurements were performed so far on the different microstructural elements of the single-phase materials or pure metals. In our previous study, we developed a surface preparation technique that allowed us to image in SFM the recrystallized grains embedded in untransformed ultrafine-grained matrix in partly recrystallized Cu [10]. Used in combination with the Triboscope nanoindenter, this technique allows separate measurements of elastic modules and nanohardnesses of newly nucleated grains and untransformed matrix. The aim of the present work is to establish a correlation between the macro- and nanomechanical properties of ultrafine-grained Cu produced by ECAP and its microstructure.

2. Experimental

The present study was performed on 99.99 wt.% Cu rods of about 200 mm in length. The major impurities in the initial material were P (26 wt. ppm), Ag (25 wt. ppm), S (10 wt. ppm) and O (4 wt. ppm). The content of other impurities was either below 1 wt. ppm or below the detection limit of the spectroscopy technique used in elemental analysis. The samples were deformed at room temperature by B_C ECAP route for four passes using an ECAP die with the angle of intersection of two channels $\Phi = 90^\circ$ and the outer angle $\Psi = 30^\circ$. In B_C route the rod is rotated by 90° in the same direction between consecutive pressings. Standard tensile specimens were machined from the samples parallel to the flow direction of the sample. Some samples were annealed in a liquid salt bath in the temperature range 250–300 °C for 30 min. One sample was annealed at 700 °C for 3 h in the atmosphere of purified hydrogen. This way fully recrystallized microstructure with the large grains (average grain size above 100 μm) was produced. The specimens were tested in tension in a Lloyd testing machine, using a ram speed of 5 mm/min. The values of strain given by the built-in strain gauge were calibrated by measuring the distance between the marks pre-scratched on the surface of the specimens before and after tensile test. The Brinell hardness was determined using a 2.5 mm ball indenter under a load of 31.25 kg. The Vickers hardness was determined with the aid of Buehler microindenter using the load of 10 g.

For transmission electron microscopy (TEM) studies the as-received and annealed rods were cut into discs of approximately 500 μm thickness, using a precision saw Accutom-5 (Struers) with an alumina cutting wheel. These discs were polished with SiC papers and diamond paste down to a thickness of 150–200 μm and cylindrical TEM samples of 3 mm in diameter were then cut out of them. These small discs were further thinned using an electrojet polisher in an orthophosphoric acid solution (density 1.37 g/cm^3) at room temperature and at an applied voltage of 2.1 V (2 mA current), for about 9 min.

TEM observations were performed using a JEOL FX-2000 microscope with LaB_6 filament, operating at 200 kV. The micrographs were obtained using conventional diffraction contrast imaging under bright-field and dark-field conditions. Selected area electron diffraction (SAED) patterns were taken from an area of 2 μm^2. The average grain size and the misorientations between the grains were measured.

The SFM measurements were performed using the Autoprobe CP of Park Scientific. Si tips coated with tungsten carbide with a nominal radius of curvature of 50 nm were used for the SFM imaging of Cu samples in the tapping mode. To prepare the surface for SFM measurements, we polished the samples on abrasive SiC papers and afterwards on diamond paste down to 1 μm particle size. Mechanically polished samples were then polished electrolytically in an orthophosphoric acid solution (density 1.55 g/cm^3) at a current density of 20 A/cm^2 for 20 min. Following electropolishing, the surface to be imaged in SFM was slightly etched in a solution of 5 g $FeCl_3$ and 30 ml HCl in 100 ml of distilled water. Due to the dependence of the etching rate on the orientation of the surface the grain microstructure of the sample should manifest itself through the differences in heights of individual grains.

Nanoindentation experiments were performed using the Hysitron Inc., Triboscope. A Berkovich indenter was employed and its shape in the vicinity of the apex was calibrated using a standard sample of fused silica. Analyses for the tip calibration and the calculations of hardness were performed by the method of Oliver and Pharr integrated in the Tribo-