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GRAIN REFINEMENT IN COPPER VIA CRYOGENIC DEFORMATION

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Abstract. The high-resolution electron backscatter diffraction (EBSD) was employed to study microstructure produced by cryogenic high-pressure torsion of copper. The long term (~11 months) thermal stability of the obtained material at room temperature was also evaluated. It has been established that severe cryogenic deformation leads to a considerable grain refinement down to 0.3 μm. However the obtained material was shown to be quite unstable exhibiting abnormal grain growth at ambient temperature.

1. INTRODUCTION

Production of nanocrystalline (NC) materials attracts significant scientific and industrial interests [1–5]. Presently, they are produced predominantly by the methods of powder metallurgy, crystallization of amorphous alloys, or deposition on a substrate [6]. These approaches, however, are characterized by a number of disadvantages, among which the limited volume of the material being obtained is one of the most substantial drawbacks. In this regard, the methods of severe plastic deformation (SPD) gain widespread application [7]. The main SPD methods include equal-channel angular (ECA) extrusion [8], multiaxial deformation [9], screw extrusion [10], and accumulative roll-bonding (ARB) [11]. However, the minimum grain size attainable by these methods is frequently larger than 0.1 μm [11,12] and thus the development of new, more effective approaches is desirable. One of them is a deformation at very low absolute temperatures, i.e. so-called cryogenic deformation [13–17]. It is assumed that cryogenic temperatures should suppress the processes of dynamic recovery/recrystallization, promote mechanical twinning (even in cubic metals [14,15], and thus intensify formation of NC structures. In several recent papers it has been shown that the cryogenic deformation promotes the grain refinement down to 0.2 μm when using ECA pressing and rolling [13–15] and even less than 0.1 μm in some cases [14,15]. However, efficiency of cryogenic deformation for grain refinement is still not completely clear and thus more studies in this field are required. In this work thermal stability of the cryo-deformed copper was evaluated.

2. EXPERIMENTAL

A commercially pure (99.9%) copper of the M1 grade was employed as the program material. The initial hot-rolled bar was cut into parts 40 mm in diameter and 70 mm long and was subjected to multiaxial deformation in a temperature range of 500–300 °C [9], giving an average grain size of ~1.7 μm. The obtained material was denoted as initial material in this paper. Samples in the form of a disk 10 mm in

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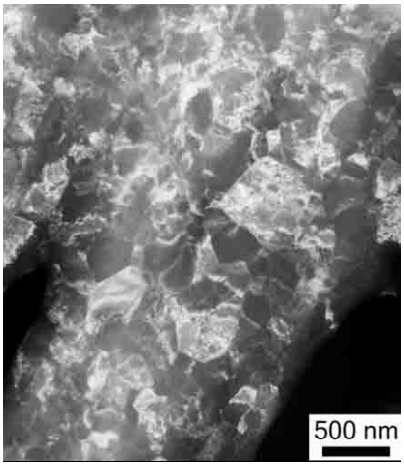

Fig. 1. TEM image of the microstructure taken ~30 minutes after cryogenic deformation.

diameter and 2 mm in thickness were cut from the central, most deformed part of the forged workpiece and subjected to cryogenic deformation via high-pressure torsion (HPT) under an applied pressure of 4.5 GPa on a Schenck universal testing machine. The reversible deformation was applied: the sample was deformed using sequential rotation of the anvil clockwise and counterclockwise through an angle of 45°. To provide cryogenic temperature conditions, the samples were cooled in liquid nitrogen immediately before strain. To prevent the rapid warming up of copper to room temperature during deformation, HPT anvils were also cooled in the liquid nitrogen. For microstructural observations, the deformed samples were electro-polished in a 7% solution of orthophosphoric acid H_3PO_4 in distilled water at room temperature at a voltage of 10 V. Microstructure developed in the material was quantified by using transmission electron microscopy (TEM) and electron backscatter diffraction (EBSD). To examine thermal stability of the material, the microstructural observations were performed after 2 weeks and 11 months of the static storage at room temperature. For TEM investigations, a Phillips CM 30 electron microscope operating at an accelerating voltage of 300 kV was employed. The EBSD analysis was carried out using TSL OIM™ software installed on a Hitachi S-4300SE scanning electron microscope with a field-emission gun. To minimize errors, each electron diffraction pattern was automatically indexed on the basis of seven Kikuchi lines. The pattern solving efficiency was ~ 99.5%. The EBSD data were subjected to automatic correcting; all fine grains consisting of 3 or fewer pixels were automatically eliminated from the EBSD maps. In view of an experimental error of the EBSD method, all

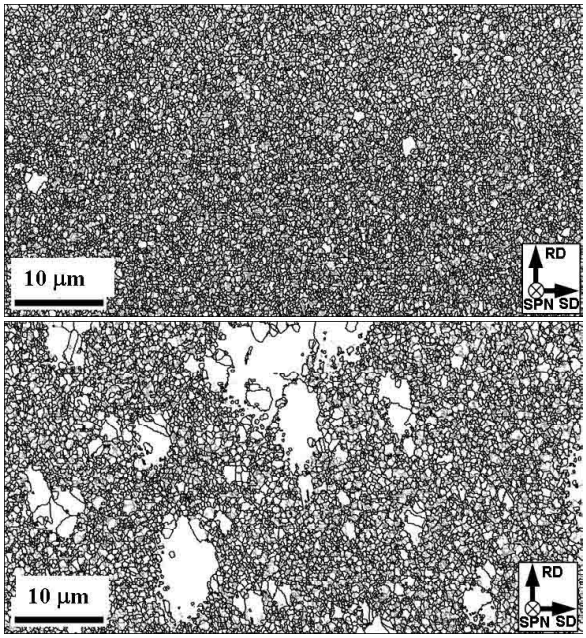

Fig. 2. EBSD maps of the microstructure after cryogenic high-pressure torsion (a) and after subsequent long-term static storage at room temperature (b). LABs and HABs are depicted as thin grey and thick black lines, respectively. RD, SD, and SPN denote the radial direction, shear direction, and shear-plane normal, respectively.

low-angle boundaries with the misorientation smaller than 2° were excluded from consideration. A 15-degree-misorientation was used as a criterion to differentiate low-angle boundaries (LABs) vs. high-angle boundaries (HABs). The linear intercept method was used for grain-size measurements.

3. RESULTS

Typical TEM image of the microstructure obtained ~ 30 minutes after deformation is shown in Fig. 1. It is seen that the structure consists of approximately equiaxed fragments the size of which ranged from 50 nm to 1 μm. Coarse grains typically contained residual substructure. The residual dislocation density appears to be high. The very narrow (~ 30 nm in width) twins were found within some fragments (not shown).

EBSD maps of the cryo-deformed copper obtained after 2 weeks and 11 months of static storage at room temperature are shown in Fig. 2. In the maps, the LABs are depicted as thin gray lines and HABs as thick black lines. The maps are presented such that the vertical axis is parallel to the radial direction of the sample, whereas the horizontal axis is parallel to the tangential direction, i.e., the direction of shear upon torsion.

The microstructure after 2 weeks at room temperature was reasonably homogeneous and consists of approximately equiaxed grains whose average grain size is ~ 0.3 μm (Fig. 2a). After 11 months at room temperature, the microstructure was noticeably different (Fig. 2b). The principal feature of the microstructure after this longer time was the appearance of a number of coarse grains within a matrix of fine grains, i.e. the microstructure had become essentially bimodal (Fig. 2b). The very large difference between the grain sizes suggests that the material had undergone abnormal grain growth. The coarse, abnormal grains were typically free of LABs, but contained some coarse rectangular-shaped twins and even sporadic, fine, unconsumed equiaxed grains (Fig. 2b). It is also noteworthy that the abnormal coarse grains exhibited a slight directionality in growth, tending to align with radial direction. It may be hypothesized that this effect is associated with the sample-scale strain gradient typical for HPT (Fig. 1), although this conjecture requires further investigation. In the fine-grain regions of the two samples grains also underwent growth, albeit of a more normal nature, between 2 weeks and 11 months at room temperature.

4. DISCUSSION

Microstructural instability at room temperature (this effect is frequently termed "self-annealing") has been observed in silver [18-22], gold [21], copper [23-30] and even in aluminum [31]. In all cases, the room temperature is very low in homological scale for these materials and therefore the self-annealing effect was rather a surprising result. The characteristic feature of this process is slow kinetic and thus the effect may only be revealed after a relatively long-term exposure – from several week [28] to several years [26]. To the best of the authors' knowledge this phenomenon is found only in pure metals and it quite expectedly becomes more pronounced with reduction of impurity level [20,24]. Typically, the self-annealing is found in materials with relatively fine-grained structure produced by ether large deformation [18-21,23-29,31] or electro-deposition [22,30]. This presumably indicates that the driving force for this process is significantly contributed by grain-boundary energy. In case of silver (and, perhaps, gold), an additional driving force arises from large dislocation density associated with low stacking fault energy in these materials [18-21]. The self-annealing effect may be manifested by recovery [18-20,29], recrystallization [18-20,23-27,29,31], grain growth [21-22,28-30], or by combination of these. In this section, the abnormal grain growth observed in our experiment is briefly discussed in terms of these conventional annealing phenomena.

The recovery seems to be the most reasonable process at room temperature which is thought should occur in any case. In Ref. [18], the kinetic of the room-temperature recovery in silver was explained in terms of probability of a cross-slip event. In cryo-deformed copper, the recovery appears as a reduction of grain-orientation spread [29] but its mechanism is not clear.

Since the recovery reduces stored energy in a material, it decreases driving force for recrystallization. It is well accepted that the size of the recrystallization nuclei is governed by a balance between their grain-boundary energy and the energy of stored dislocations eliminated by the formation of the nucleus. In Ref. [29], it was shown that the minimal size of stable recrystallization nucleus in the cryo-deformed copper may be as large as 2 μm. This is much larger that the mean grain size (Figs. 1 and 2a) and therefore the "classical" recrystallization via nucleation and growth seems to be impossible in this material.

In Ref. [29], it was shown that the ultrafine-grains of the cryo-deformed copper first coarsen continuously (compare fine-grained matrix in Figs. 2a and 2b) and simultaneously recovery takes place in grain interior. Once a size of the recovered grain exceeds the minimal size of stable recrystallization nucleus, it gains an advantage in grain growth. Due to the inhomogeneous distribution of stored energy in different grains, the recovery process is expected to be spatially heterogeneous, and the number of stable nuclei would be expected to be small. In this situation, the recrystallization may degenerate into a catastrophic growth of a few selected grains, as observed in Fig. 2b.

Another possible reason for the observed abnormal grain growth is annealing twinning. It is known that grain-boundary migration in copper may gives rise to twins. These twins are defect-free and are outlined by highly-mobile S3 twin boundary; this may provide an advantage in grain growth. Crystallographic measurements have shown that the fine-grained matrix in Fig. 2b has {*hkl*}<110> fiber texture with pronouced $B/\bar{B}$ $(1\bar{1}2)[110]/(\bar{1}1\bar{2})[\bar{1}\bar{1}0]$ simple-shear texture component; in contrast, the preferential orientation of the abnormal coarse grains is rather close to {100}<100> cube texture [162]. As noted by Verbraak [33], the crystallographic orientations of {112}<110> and {100}<100> and are nearly twin-interrelated and therefore the abnormal coarse grains may originate from annealing twins.

5. CONCLUSION

The severe cryogenic deformation of copper has been found to lead to very poor microstructural stability. Both normal and abnormal grain growth occur during prolonged exposure at room temperature following such processing. The abnormal grain growth is assumed to be attributable to a specific character of self-annealing effect in ultrafine-grained materials. Thus, cryogenic deformation can hardly be an effective means for obtaining an NC state in copper.

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