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Microstructural evolution and mechanical properties of nanostructured copper

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Abstract. Nanostructured metallic materials exhibit outstanding mechanical properties. Pure copper was chosen as a test material and was subjected to an equal channel angular pressing to produce a nanostructure. The paper analyses development of the microstructure during severe plastic deformation of copper and mechanical properties of the metal. Tests show that the nano-cristalline copper possesses high tensile strength and microhardness as well as high plasticity after hard cyclic viscoplastic deformation. However, heat treatment and method of deformation influence the properties to a large extent. Dependence of the changes in structural parameters and properties on the deformation process and heat treatment are studied.

Key words: nanocrystalline copper, nanostructure, mechanical properties, severe plastic deformation.

1. INTRODUCTION

Many advanced technologies can usually be traced back to history. Since the pioneering experiments of Bridgeman [1] in the 1940s and 1950s, much attention has been paid to the investigation of physical aspects of high pressure and to the application of special deformation techniques. Recently, the severe plastic deformation (SPD) method of equal channel angular extrusion (ECAE) technique was invented by Segal [2]. This method has been used for fabrication of ultra-fine grained (100–1000 nm) and nanostructured (0–100 nm) materials [3]. At the present time, the SPD techniques have become a well known and extensively used approach in nanostructured materials processing.

Several methods are now available for producing ultra-fine grained and nano-crystalline metallic materials by high strain rates as high pressure torsion, cyclic extrusion–compression, multi-axis forging, accumulative roll bonding and the method of equal channel angular pressing (ECAP) [3]. Nowadays the last method has been widely used for fabrication of nanostructured materials [4,5]. Details of the ECAP procedure are given in [6,7].

It has been established that severe plastic deformation results not only in the decrease in grain size at the simple shear stress but also in the enhancement of mechanical properties of the heavily deformed materials [8–10]. However, increase in the yield stress is accompanied by a drop in ductility [11]. In contrast to many materials [12,13], nanostructured copper possesses both high strength and high ductility as a result of appropriate heat treatment. At the same time, data in [14,15] show a significant scatter in the values of the mechanical properties of pure copper depending on the structure. Moreover, for complete understanding of the material behaviour, hardening/softening under hard cyclic viscoplastic (HCV) deformation and subsequent tension loading up to a total fracture [16], the evolution of the microstructure and stresses should be considered in detail. Some theoretical models, concerning the strengthening/softening mechanism in nano-crystalline metals under high-strain-rate superplastic deformation, are proposed in [17]. Plastic deformation and strain hardening mechanisms are discussed in [18].

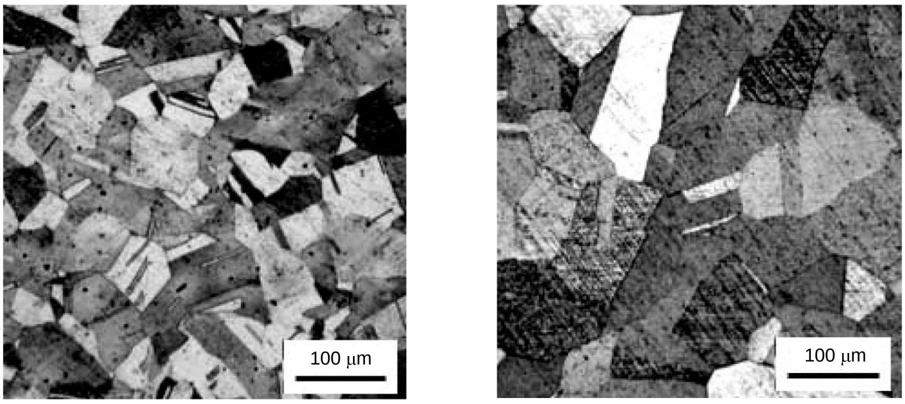
The main aims of the present study are investigation of the microstructural features of severely deformed pure copper, processed with the ECAP method, and examination of mechanical characteristics of nanocrystalline pure copper after different processing modes.

2. MATERIAL AND EXPERIMENTAL PROCEDURE

Technically pure copper was used as a face-centered cubic material. Micro-structure of cold drawn copper is shown in Fig. 1a and microstructure of annealed pure copper, used as the initial material, in Fig. 1b. Table 1 lists the mechanical properties of the cold-worked copper and annealed copper after recrystallization at the temperature of 650 °C and heat treatment during 1.5 h.

The procedure of ECAP consists of using a special die, containing two channels of equal cross-sections and intersected at an angle of 90°. A cylindrical specimen, subjected to SPD, was prepared from an annealed pure copper bar with a diameter of 16 mm and length of 150 mm. Each ECA pressings was conducted in air at room temperature by application of a load of about 30×10^4 N following a route B_C. Maximum 11 ECAP passes were used in this study.

Following the ECAP method, specially prepared sample segments were subjected to microstructural analysis using the optical microscope (OM) Nikon CX and scanning electron microscope (SEM) Gemini, LEO, Supra 35 and X-ray Diffractometer D5005, Bruker. Based on the X-ray investigation, the mean size of nanocrystallites was computed with the WIN-CRYSIZE program.



(a) (b)

Fig. 1. Optical micrographs of the microstructure of the pure copper in cold-drawn condition (a) and after homogenized heat treatment at 650 °C, 1.5 h (b).

Table 1. Mechanical properties of copper

Structure state	Mean grain size, μm	Vickers hardness HV10	Microhardness, HV0.05	Ultimate tensile stress $\sigma_{0.2}$, MPa
Cold drawn	~100	103	98 ± 12	270
Annealed	~200	48	63 ± 1	27

For the measurement of the mechanical properties, the tester Zwick Z2.5/TS1S was used, applying a microindentation method according to the standard EVS-EN ISO14577-1:2003. Microhardness of the materials was measured at a load of 50 g and testing time of 12.5 s with the Mikromet-2001 tester. The tension stress and ductility were tested with Automated Materials Testing System INSTRON 8516 after HCV deformation [16]. A specimen 30 ± 0.2 mm long and 10 ± 0.05 mm in diameter was stressed in tension–compression of HCV deformation. An extensometer with base length of 25 mm was used for strain measurements. Tensile straining was carried out at room temperature of about 23 °C and humidity of 40% under the sample rate of 3.000 pts/sec, and ramp rate of 0.03000 mm/sec.

3. RESULTS

3.1. Examination of the microstructure

Examination of the microstructure of the severely plastically deformed copper after the very first ECAP pass shows a grain size reduction (Fig. 2, a and b) and the forming of slip lines. Gross plastic deformation of a polycrystalline specimen corresponds to the distortion of the individual grains by means of slip (Fig. 2a).

The grains become elongated along the direction, in which the specimen was extruded. The grain width or mean deformation bands width differs from one grain to another to a large extent and varies from 2 to 20 μm (Fig. 2a).

High density of dislocations in large grains results in the well-developed dislocation cell structure in the severely deformed material. After the localized deformation introduces shear bands, the interactions of dislocations produce dislocation walls that lead to the formation of new grain boundaries and, consequently, to the creation of new nanoscaled grains. There are low- and high-angle boundaries within a shear band. However, the high-angle grain boundaries prevail between grains in neighbouring bands (Fig. 2, b and c).

The microstructure of copper in the SPD zone shows characteristic shear bands in the zone of deformation. The new formed grains have a size of about 200 nm.

The nanostructure of heat-treated copper after 11 passes of ECAP via route B_C is shown in Fig. 3. Two of the cube sides illustrate grain arrangement in the longitudinal direction along the axis of the bar, and one shows a structure in perpendicular directions.

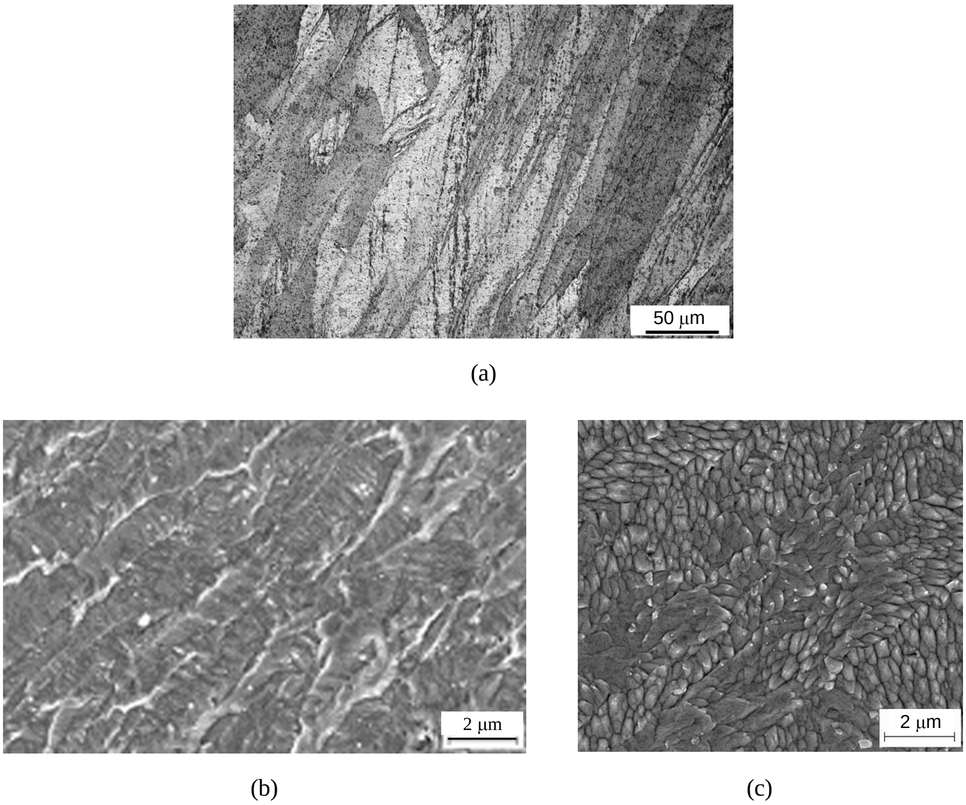
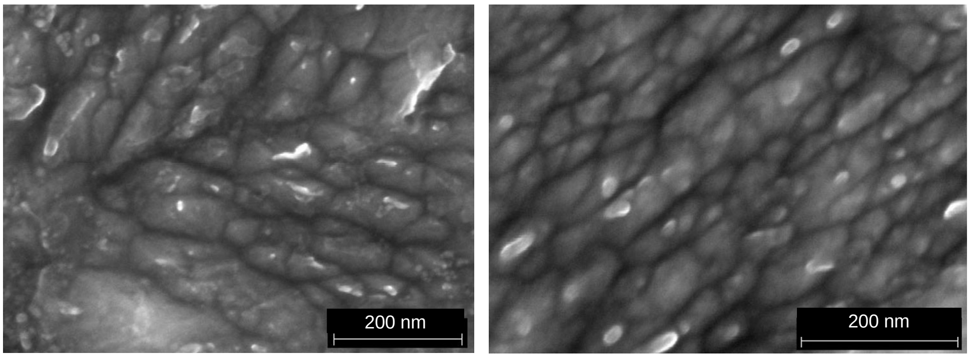


Fig. 2. OM (a) and SEM (b, c) micrographs of the refining of large grains and shear band formation after the first pass of ECAP.

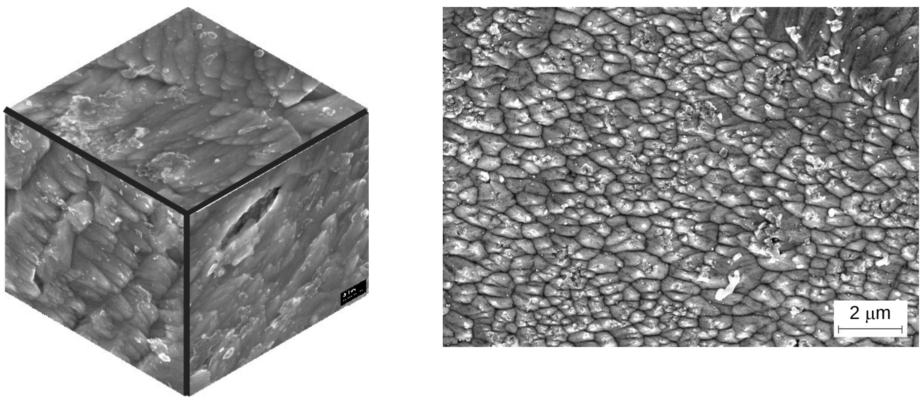


(a) (b)

Fig. 3. SEM micrographs of nanocrystalline copper in cross-section (a) and in longitudinal direction of specimen or direction of metal flow by SPD (b).

The microstructure of copper, subjected to ECAP, is shown in Fig. 4. The common view of the structure subjected to additional deformation is not changed significantly. However, the X-ray testing indicates a decrease in grain size to 39.9 nm after 11 passes of ECAP. Moreover, the tangled structure of grain boundaries becomes more evident. In the longitudinal plane, the grains are oriented at about 45° to the axis of extrusion.

Several studies, concerning the refinement of grains during SPD, have been already published [5,11,12]. As it can be seen from micrographs, presented in this paper, the microstructure of heavily deformed metal consists of nanosized ellipsoidal grains, separated by high-angle boundaries. It is worth noticing that the grain size, measured and calculated by XRD technique, is less as compared with the grain size, estimated by means of SEM micrographs analyses.



(a) (b)

Fig. 4. Microstructure of pure copper after 11 pressings through the die via route B_C (a) and SEM micrograph of the copper microstructure after 11 ECAP passes and heat treatment at 200 ºC (b).

3.2. Examination of the hardness

Table 1 presents the dependence of the Vickers and microhardness of the initial metal on the structure. It is well established that the hardness of nano-grained materials is significantly higher than the hardness of the coarse-grained ones. The variation of the microhardness with the number of ECA pressings is shown in Fig. 5. ECAP leads to a significant increase in microhardness just after the very first pressing and, for example, after 5 passes the hardness becomes 220% of the initial. However, the increase in hardness is not as significant after some passes as it is after the two first ones. SEM micrograph of the copper microstructure after 11 ECAP passes is shown in Fig. 4b.

Increase in the universal and plastic hardness in the SPD region during the first ECAP pass is shown in Fig. 6. The first pressing results in the formation of slip bands (Fig. 2, a and b) under simple shear stress. The universal hardness

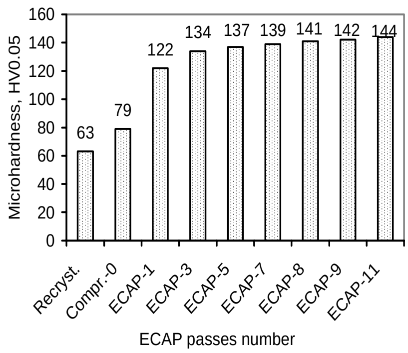


Fig. 5. Effect of SPD on pure copper microhardness (Recryst. – copper after recrystallization; Compr.-0 – copper after compression with no SPD; ECAP – 1…11 – copper subjected to a number of ECAP passes).

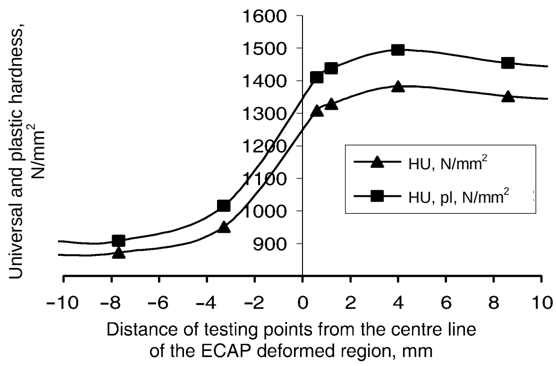


Fig. 6. Universal hardness after the first pass of ECAP in SPD region.

(HU) is increased up to 1.5 times, while increase in the plastic part of the universal hardness (HU_{plast}) is higher, up to 1.7 times. Hardness value depends on the development of the structure.

The hardness has achieved its maximal value on a distance of about 4 mm from the centre line of SPD. Slight decrease in hardness is caused by the temperature increase in the region and, consequently, by the increase in the relaxation process [10].

3.3. Tensile testing

It is well established that the SPD method allows to obtain materials with enhanced mechanical properties, first of all, with a high value of yield strength. However, materials, stressed plastically, often exhibit low ductility [11]. The representative engineering stress–strain curves for copper, subjected to different technological treatments, are shown in Fig. 7.

Coarse-grained copper (N2A), annealed at 650 °C and not HCV deformed, has the lowest tensile strength of 215 MPa but elongation to failure is large enough and equals to 82%. HCV deformation results in a 10% strain decrease at 1 + 2 + 1% loading (N2) and in 15% strain decrease at 2 + 1% loading (N2B). According to [10], the stress at strain 0.2% ($\sigma_{0.2}$ = 20 MPa) is minimal and the Young modulus is lowest for the metals stressed in HCV. Annealed coarse-

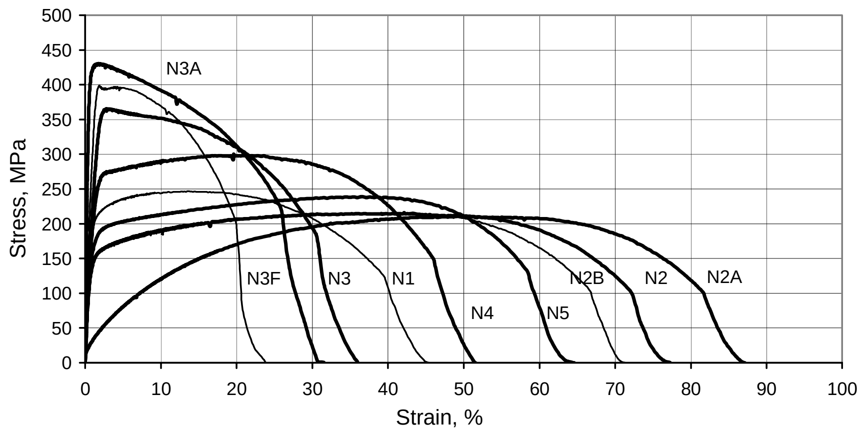
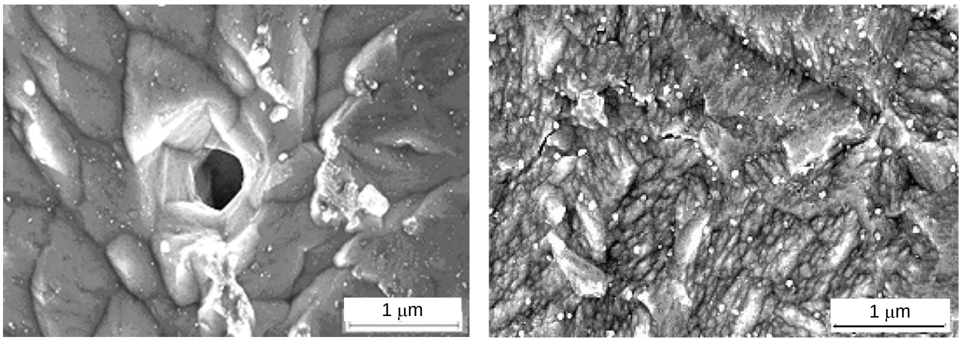


Fig. 7. Ultimate tensile stress–strain diagram of pure copper specimens after HCV axial deformation [16] at 1 + 2 + 1% and 30 cycles for different structures: N1 – cold-drawn; N2 – annealed at 650 °C for 1.5 h; N3 – nanocrystalline, with crystallite size (CS) of 40.5 nm; N4 – nanocrystalline copper after heat treatment at 200 °C and heating rate of 1 °C/s, and CS = 71.7 nm; N5 – similar to the specimen N4 but heat treated at 400 °C with heating rate of 2 °C/min and CS = 101 nm, HCV deformed at 1 + 2%; N2B – annealed at 650 °C for 1.5 h, HCV deformed at 2 + 1%; N2A – similar to N2B but with no HCV deformation; N3F – nanocrystalline copper after cold die forging from the diameter of 16 to 8 mm and CS = 74 nm; N3A – nanocrystalline copper with CS = 40 nm with no HCV deformation.



(a) (b)

Fig. 8. Microstructure of the heat-treated nanocrystalline copper (N4) at neck area before fracture: (a) pore forming; (b) crack forming.

grained copper shows the maximum increase in tension stress that gives an evidence of copper strain hardening during tensile loading (N2A). The nano-crystalline pure copper shows a very small degree of strain hardening (N3, N3F, and N3A) during tension. The coarse-grained copper at cold-drawn condition of HCV deformation shows only softening behaviour [16], the stress increasing cause the hardening up to strain of 15% (N1). ECAP significantly increases the tensile strength of material up to maximum of 430 MPa for the N3A speci-men. The price of this enhancement of strength is the reduction of the ductility of the metal. The nanocrystalline copper (N3F) after cold die forging and HCV deformation possesses the lowest strain (20%) up to total fracture. Heat treat-ment at low heating rate of 1 °C/min and 200 °C leads to an increase in crystallite size from 40 to 72 nm for nanocrystalline copper (N4) and increasing of the crystallite size influences the maximal tension stress value, which is decreased from 430 to 300 MPa or for 33% from the maximum. The strain at total fracture is increased from 25 to 46 or for 84% (N3A and N4). The true fracture stress of heat-treated at 200 °C pure copper specimen is increased up to 1800 MPa [16]. The double heat-treated specimen (N5) possesses the highest strain hardening in tension up to the stress of 240 MPa and the strain at total fracture is increased up to 58% (N5).

Figure 8 shows the material at the zone of extensive deformation at the neck. The flaw formation and microcracks nucleation can be seen.

4. DISCUSSION

The change in material behaviour after being subjected to SPD suggests a change in the mechanisms of deformation. Plastic deformation of coarse-grained metals mostly corresponds to the motion of large numbers of dislocations and twinning. Grain boundary structure is particularly important in nanomaterials, for which the grain boundary to grain volume ratio is high. There are a lot of high-angle grain boundaries that impede the dislocations motion and result in the decrease in the average distance between dislocations. These features lead to the hindering of the dislocation motion and consequently to the enhancement in strength. Simultaneously grain boundaries open up several effective deformation modes that usually are not available in coarse-grained polycrystals. These modes are grain boundary sliding [9,13], diffusion creep of grain boundaries [14] and rotation [15].

Some fraction of the energy, expended in deformation, is stored in the metal as strain energy. The appropriate heat treatment may revert back to the pre-cold-worked states. During heating, some of the stored energy is relieved by virtue of dislocation motion and there is a reduction in the number of dislocations.

The heat treatment at 200 °C (N4) and 400 °C (N5) allows some recrystallization process to occur and an increase of the grain size. The metal becomes weaker but more ductile and the thermal stability of the nanostructured material increases significantly [16,19]. Therefore, understanding of the material behaviour on different stages of processing may allow to tailor the mechanical properties and to design new materials needed for any applications.

5. CONCLUSIONS

The development of the structure of pure copper during different processing modes influences mechanical properties of the metal.

1. At the first pass of ECAP, the large equal-axis grains are severely deformed and sub-grains with high-angle boundaries are formed in the slip bands. Refining of the grain size results in a significant increase in the hardness.
2. Increase in the tensile stress and hardness are maximal at the very first pass of ECAP. Nanograined microstructure is developed at the first ECA pressing.
3. Increase in the number of ECAP passes results in a slight enhancement in the properties of the material as compared to the very first ECAP; however, relaxation increases with the increase of the number of passes.
4. Heat treatment has stabilizing influence on mechanical properties and grain growth and also on relaxation processes in the grain–boundary structure.
5. Tensile HCV deformation influences the growth of nanograins and the orientation of grains in the metal along the direction of load application.
6. HCV deformation causes a decrease of the strain in the annealed metal and an increase of the strain and a decrease of the Young module in the nano-crystalline material.

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Nanostruktuurse vase evolutsioon ja mehaanilised omadused

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Nanostruktuursed materjalid on suurepäraste mehaaniliste omadustega. Artiklis on uuritud puhta vase mikrostruktuuri evolutsiooni sügaval plastsel deformatsioonil võrdkanalilise nurkpressimise meetodil. Mehaaniliste omaduste uurimine näitas, et nanokristalsel vasel on suur tõmbetugevus ning mikrokõvadus ja hea plastsus isegi pärast intensiivset tsüklilist viskoplastset deformatsiooni. On uuritud ka struktuuriparameetrite ja mehaaniliste omaduste muutumist sõltuvalt deformatsiooniprotsessidest ja kuumtöötlemisest.