

## Producing bulk nanocrystalline materials by combined hydrostatic extrusion and equal-channel angular pressing

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Nickel and copper were subject to severe plastic deformation at room temperature, using hydrostatic extrusion (HE) and equal-channel angular pressing (ECAP). The maximum deformation was 13.5 in nickel and 22.3 in copper. These deformations were obtained by each of the techniques separately and by their combination. It has been found that the combined HE and ECAP deformation greatly increases the homogeneity of the microstructure and improves considerably its mechanical properties comparing with a single technique. After the combined treatment, the grain size of both copper and nickel was of the order of 100 nm. The experiments have shown that the combination of HE and ECAP techniques permits producing homogeneous nanocrystalline materials of large volumes.

*Key words: severe plastic deformation; hydrostatic extrusion; nanocrystalline structure; grain refinement; nickel; copper*

### 1. Introduction

Severe plastic deformation (SPD) applied to metals and alloys yields solid materials with a nanocrystalline or ultrafine grained structure [1]. Formation of such structures results in a considerable improvement of the mechanical properties of materials. A very high mechanical strength is usually accompanied by a reserve of plasticity on a level unachievable with classical techniques employing conventional hardening me-

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thods [1–3]. Among the most popular SPD techniques there are high-pressure torsion (HPT) and equal channel angular pressing (ECAP) [1, 2, 4–7]. Recently, fabrication of nanocrystalline metals via the SPD techniques has increasingly been concentrated on combinations of these two techniques [2, 8]. By combining the SPD techniques, one can increase the deformation degree and alter plastic deformation paths which results in more fine-grained structures and improved mechanical properties. The authors of Ref. [9–12] have recently reported on successful experiments with the use of hydrostatic extrusion (HE), conducted at room temperature, for fabricating nanocrystalline (NC) and ultra-fine-grained (UFG) structures in titanium, Al-alloys, iron, 316LVM steel and copper.

The aim of the present study is to describe structures produced by a combination of ECAP and HE. This was achieved for nickel and copper widely used in electronics. Because of its plasticity and the microstructural homogeneity, nanocrystalline nickel may replace electro-plated nickel used in MEMS circuits thus far [8–14]. Nanocrystalline copper, on the other hand, may be used instead of gold in electronics, thereby reducing costs and eliminating the purification and doping processes [12].

## 2. Experimental

Purity of nickel used in the experiments was 99.98%, and that of copper – 99.8%. The SPD parameters employed are given in Table 1. The ECAP process was conducted in a 90° die by route  $B_C$  in eight passes for nickel and sixteen passes for copper. The HE process was carried out in a cumulative manner until the final diameter was reduced to 3 mm, with the total length of the product of about 350 mm. Both materials after HE have been water quenched to reduce recovery. Both processes were conducted at room temperature. The deformation rates for HE varied between 9 and  $3 \times 10^2 \text{ s}^{-1}$ , whereas in the ECAP process  $8 \times 10^{-2} \text{ s}^{-1}$ . The starting microstructures were analyzed using optical microscopy and, after the SPD by transmission, electron microscopy at the accelerating voltage of 120 kV. A quantitative analyses of the images obtained (grain size distributions) were performed using the “Micrometer” software. The mechanical properties were determined by tensile tests conducted at room temperature at a strain rate of  $2 \times 10^{-3} \text{ s}^{-1}$ . HV0.2 (15 s) of the materials subject to combined SPD treatment was also measured.

Table 1. The deformation path layout

Type of SPD	Cu true strain	Ni true strain
ECAP	18.4 (16 passes)	9.2 (8 passes)
HE	5.65	4.6
ECAP + HE	22.3	12.4 <sup>a</sup>
HE + ECAP + HE	–	13.5

<sup>a</sup>Presented in [3].

### 3. Results and discussion

#### 3.1. Investigations of microstructure

The starting average grain size of copper was  $250\ \mu\text{m}$  with the standard deviation  $SD = 60\ \mu\text{m}$ , and for nickel  $50\ \mu\text{m}$  with  $SD = 18\ \mu\text{m}$ . Both materials were characterized

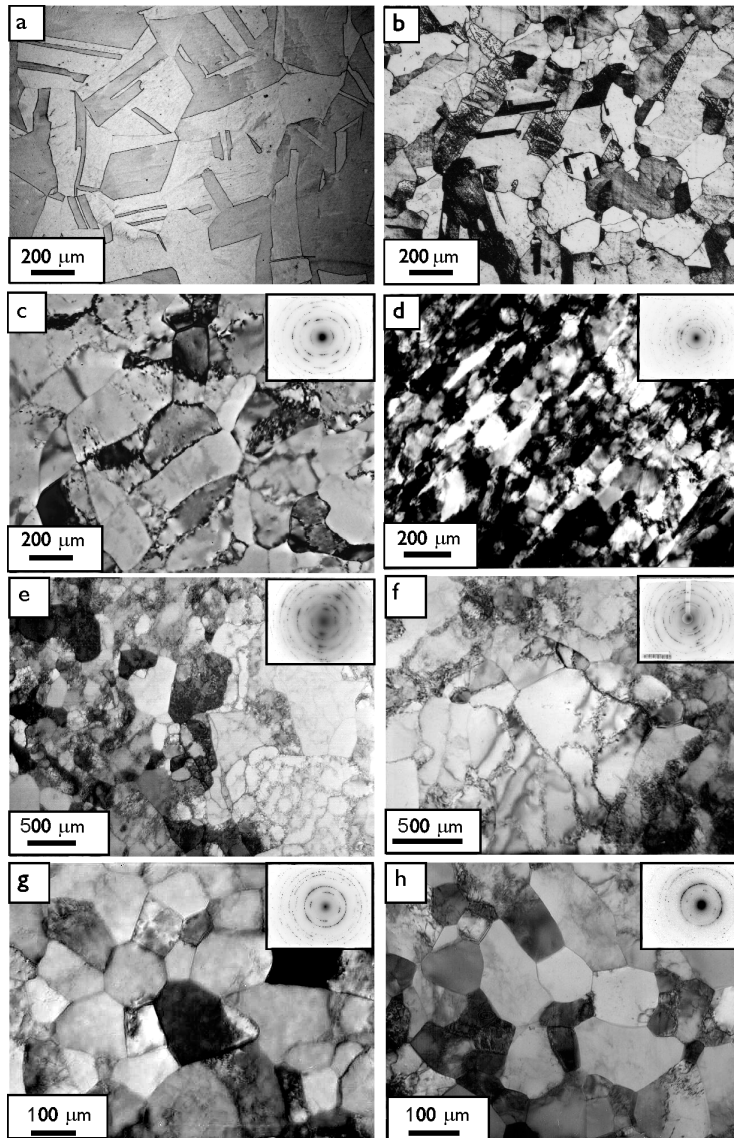


Fig. 1. Microstructures of copper and nickel: a, b) starting state, c, d) after ECAP – 16 passes for copper and 8 passes for nickel, e, f) after HE, g) after combined HE + ECAP (16 passes) for copper, h) after HE + ECAP (8 passes) + HE for nickel

by the presence of deformation twins (Figs. 1a, b). After ECAP, the microstructures of both copper (Fig. 1c) and nickel (Fig. 1d) showed a high degree of heterogeneity. The diffraction images and observations at various angles reveal low-angle grain boundaries, embedded into the initial grain matrix. The diffraction images of the ECAP-processed samples (Figs. 1c, d) suggest preferred crystallographic direction of the grains. In copper, we can see a dislocation structure in the form of sub-grains with the average size of about 250 nm. In nickel, apart from the considerable domination of low angle boundaries, there is a strong localization of deformation in the form of deformation bands (Fig. 1d). The average grain (sub-grain) size in the ECAP nickel was about 400 nm. A similar size was obtained for the HE nickel. In copper, both HE and ECAP, the average grain (subgrain) size was about 250 nm. Figure 1e clearly shows strong heterogeneity of the microstructures. Small grains (crystallites) formed as a result of severe deformation are mixed with regions of a subgrain structure. In both materials, ECAP and HE applied separately resulted in non-homogeneous structures. Similar results have been reported in [15]. Hence the idea was developed to combine the HE and ECAP to increase deformation degree, and after the deformation path to bring about activation of additional slip systems.

Table 2. Grain size copper and nickel after various deformation paths

State	Cu	Ni
Initial	250 $\mu\text{m}$	50 $\mu\text{m}$
ECAP	250 nm <sup>a</sup>	400 nm <sup>a</sup>
HE	250 nm <sup>a</sup>	350 nm <sup>a</sup>
ECAP + HE	120 nm	160 nm
HE + ECAP + HE	-	100 nm

<sup>a</sup>Grain/subgrain

With copper, the hydrostatic extrusion was preceded by an ECAP process, with the true strain of 22.3, whereas in nickel, the combined process included the HE + ECAP + HE sequence with a total strain of 13.5. In our earlier study, we experimented with deforming nickel using the ECAP + HE combination [3]. The experiment with double change of the deformation technique aimed at examining how the changes of the deformation path affect the properties of the material.

In copper, the combined ECAP + HE process resulted in an abrupt refinement of the microstructure (Fig. 1g) down to grain size of 120 nm. The refinement was accompanied by microstructure homogenization. The diffraction images suggest that grains are predominately surrounded by high-angle boundaries, which was also confirmed by dark field observations.

The grains shown in the micrographs are equiaxial also in nickel. By changing the deformation path twice and applying a strain of 13.5, nickel was obtained with an average grain size of 100 nm. This material contained a large number of high-angle boundaries. The nickel structure produced by a combined ECAP + HE treatment, re-

ported earlier by the present authors [3], was built of equiaxial grains 160 nm in size. Therefore, the double change of the deformation path, reported in the present paper, resulted in an additional refinement of the structure by about 60%. One can also expect the same with Cu, although the structure obtained in the present experiments already is one of the finest reported in the literature.

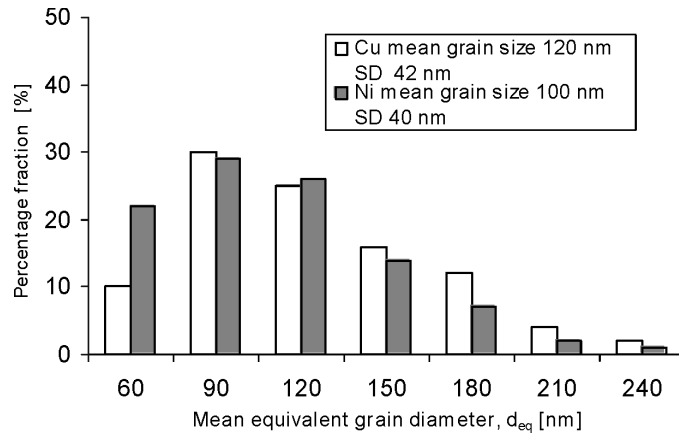


Fig. 2. Grain size distribution in nickel and copper after combination of ECAP (16×) + HE (Cu) and HE + ECAP (8×) + HE (Ni)

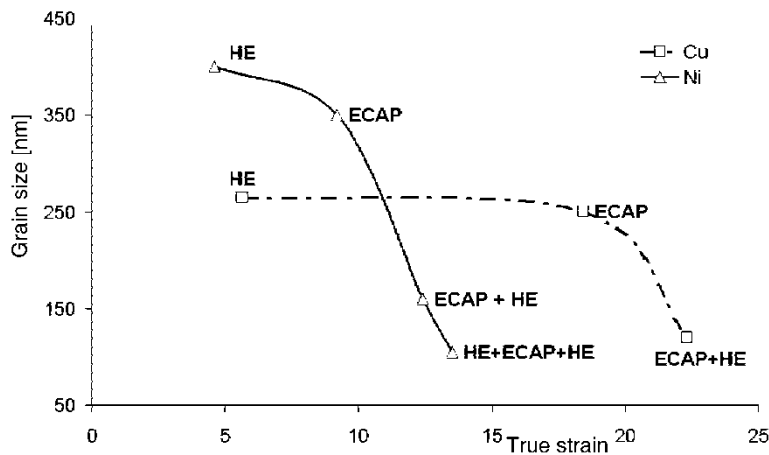


Fig. 3. Structural changes in nickel and copper as a function of true strain

Figure 2 shows the grain size distributions in the materials examined. It should be noted that the grain size distributions in nickel and copper reveal similar characters. In both, there is a certain population of crystallites, of grain sizes below 60 nm, whereas the average grain sizes are similar (100 nm and 120 nm). In spite of a considerable difference in the starting grain sizes, nickel and copper exhibited after treatments similar grain sizes and a similar degrees of homogeneity (the same standard deviation).

Some differences in the behaviour of both materials can be seen when analyzing the structural changes as a function of true strain (Fig. 3). In both materials, a strain of about 5 brings about a clear departure from initial structures. At the first stage of straining, the grains (subgrains) acquire a size which changes only slightly with increasing strain, irrespective of which SPD technique (ECAP or HE) is applied. The materials show 'saturation' and undergo only minimum changes as seen in the diagrams of Fig. 3. It is only the change of SPD process which, by changing the deformation path, gives a structure undergoing further abrupt refinement. For copper, the 'plateau' as function of strain is much longer than in nickel. This is associated with the dynamic recovery which occurs in copper at lower temperatures.

### 3.2. Mechanical properties

The results of mechanical test for nano-copper and nickel are shown in Tables 3 and 4, respectively. In both materials, the mechanical strength increases with increasing deformation. The strength is higher in the material subject to HE than in the material after ECAP, although HE accumulated strain is almost three times lower. This can be attributed to the different straining rates which in HE are much higher than in ECAP.

Table 3. Mechanical properties of copper at initial state and after various deformation paths<sup>a</sup>

State	True strain	UTS [MPa]	YS [MPa]	$\epsilon$ [%]
Initial	0	290	280	16
HE	5.56	466	460	12
ECAP	16	395	390	10
ECAP + HE	23	550	530	9

<sup>a</sup>UTS – ultimate tensile stress, YS – yield stress,  $\epsilon$  – elongation.

Table 4. Mechanical properties of nickel in the initial state and after various deformation paths<sup>a</sup>

State	True strain	UTS [MPa]	YS [MPa]	$\epsilon$ [%]
Initial	0	320	270	38
HE	4.6	946	926	15.0
ECAP	8	780	630	20
ECAP + HE [3]	11.2	1200	1120	9.5
HE + ECAP + HE	12.3	1255	1180	11

<sup>a</sup>UTS – ultimate tensile stress, YS – yield stress,  $\epsilon$  – elongation.

These two processes, HE and ECAP, also differ in the strain components. In ECAP we have pure shear, whereas in HE – a three-dimensional compressive strain state. The combined HE and ECAP process gives an abrupt increase of the material

strength. In copper, the yield strength in comparison to the initial one increases by 90%, whereas in nickel, when treated by a HE + ECAP + HE process – by 340%. This is due to the lower propensity of nickel to dynamic recovery. In both materials, in spite of the abrupt increase of strength, a relatively high plasticity of about 10% still remains.

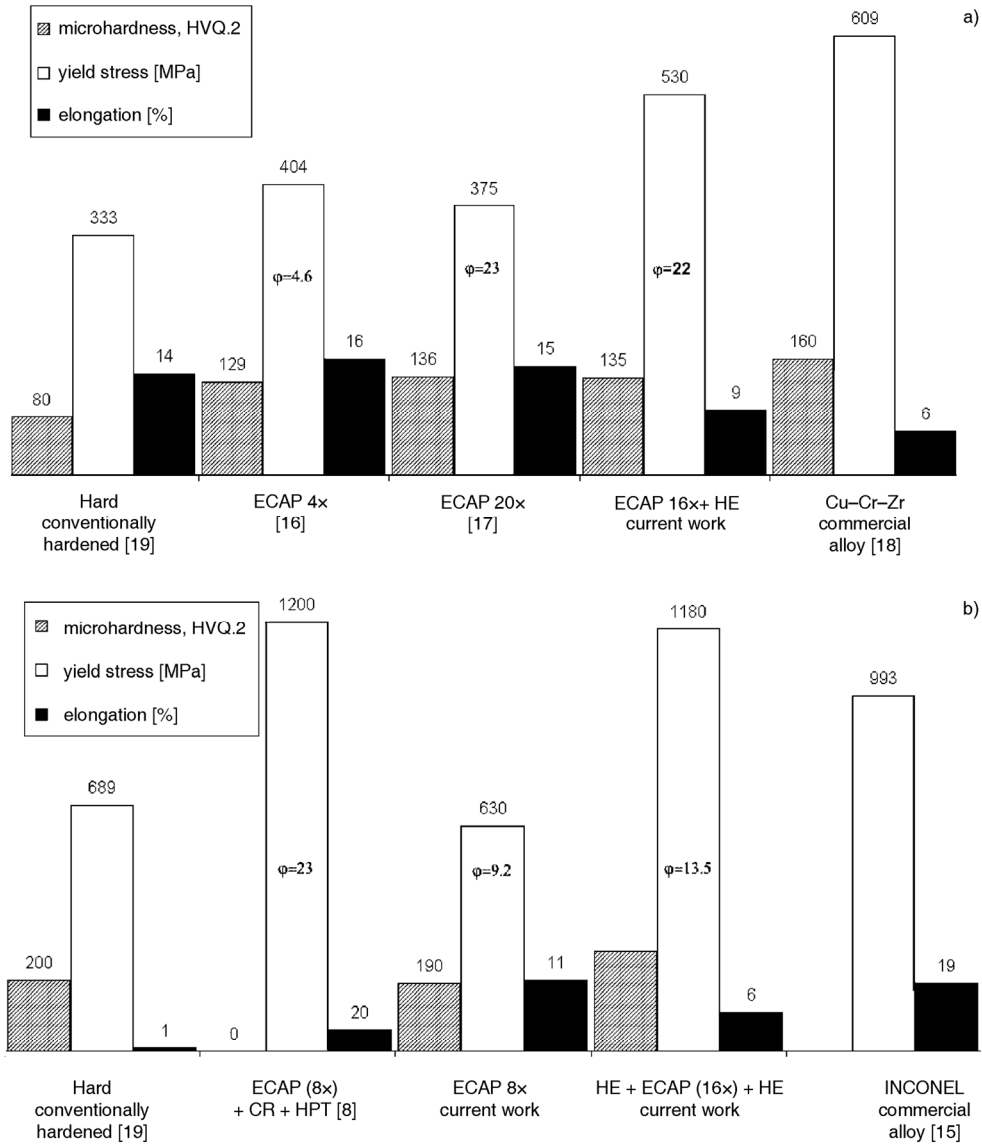


Fig. 4. Comparison between properties of a) copper and b) nickel after application of various deformation methods and commercial base Ni and Cu alloy (HE – hydrostatic extrusion, ECAP – equal channel angular pressing, HPT– high pressure torsion, CR – cold rolling,  $\varphi$ – cumulative true strain

In comparison to a coarse-grained copper strain hardened in a conventional way (Fig. 4a), the ECAP and HE Cu exhibit a similar level of plasticity. For nickel treated by the combination of HE + ECAP + HE, elongation is drastically higher than that observed for coarse-grained material hardened conventionally which shows only the elongation of 1%. The strength obtained here for copper is much higher than those reported in the literature. It is worth noting that at a similar strain applied by ECAP alone [17], the yield point is lower by 40% than that achieved when using the ECAP + HE combination. This confirms that an alteration of the straining technique during the deformation process has a crucial effect on the properties of the material. It should be noted that the strength of pure copper processed here is comparable with the high-strength alloying copper commonly used for the fabrication of welding tips [18]. The results obtained for nickel were compared with those obtained by HPT [8]. The yield stress is on the same level but after the ECAP + HE treatment the elongation is almost twice larger. Moreover, HPT permits treating products of much smaller volumes. The pure nanocrystalline nickel produced by the HE + ECAP + HE combination has the yield point higher than the popular super-strong nickel superalloy known commercially as INCONEL (Fig. 4b).

#### 4. Concluding and remarks

HE and ECAP processes applied separately to nickel and copper brought about an abrupt increase of the strength properties of these materials. However, their structures were non-uniform, with deformations and sub-dislocation structure. Double and triple combinations of two techniques (ECAP, HE) lead to an increase of the deformation degrees and changes of the deformation paths, yielding copper and nickel with homogeneous microstructures with equiaxial grains. In both materials, the 100 nm grain refinement was obtained. This strong refinement resulted in a great improvement of the strength to the level of high-strength commercial alloys. In nickel, the best mechanical properties were obtained by using a combined HE + ECAP + HE treatment under a total true strain of 13.5 (yield stress  $YS = 1180$  MPa), whereas in copper subjected to a combined ECAP + HE treatment at a true strain of 22.3, the yield stress was 530 MPa. Both materials preserved a useful plasticity (Ni – 11%, Cu – 9%) unachievable by conventional techniques of strain hardening.

The present experiments enabled developing a technology for production of nanocrystalline Ni and Cu with properties superior to those obtained by traditional SPD techniques, such as ECAP or HPT. The materials fabricated by the proposed technology can be used in micro-electronics (MEMS) for micro-elements intended to carry mechanical loads (Ni), junctions and other electronic components (Cu). This, however, requires further studies of their electrical properties.

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