A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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# ULTRAFINE GRAINED STRIPS OF PRECIPITATION HARDENED COPPER ALLOYS

# TAŚMY ZE STOPÓW MIEDZI UTWARDZANYCH WYDZIELENIOWO O MIKROSTRUKTURZE ULTRADROBNOZARNISTEJ

Precipitation strengthened copper belongs to a group of functional and structural materials applied where combination of high electrical conductivity with high strength is required. A growing trend to use the new copper-based functional materials is observed recently world-wide. Within this group of materials particular attention is drawn to those with ultrafine grain size of a copper matrix.

This study was aimed to investigate mechanical properties and microstructure in strips of age-hardenable copper alloys processed by continuous repetitive corrugation and straightening (CRCS).

Tests were performed on 0.8 mm thick, CuCr0.6 and CuNi2Si1 alloys strips annealed at 650°C for 1 hour. The specially designed construction of die set (toothed rolls and plain rolls set) installed on tensile testing machine was applied for deformation process. The changes of mechanical properties (HV, ultimate tensile strength, 0,2 yield strength) as well as microstructure evolution versus number of deformation cycles were studied. The microstructure was observed with optical and electron microscopes (TEM and SEM equipped with EBSD).

The CRCS process effectively reduced the grain size of CuCr0.6 and CuNi2Si1 alloys strips, demonstrating the CRCS as a promising new method for producing ultra-fine grained metallic strips.

*Keywords*: copper alloy, severe plastic deformation, microstructure, mechanical properties

Stopy miedzi utwardzane wydzieleniowo należą do grupy materiałów konstrukcyjnych stosowanych w sytuacji, gdzie wymagana jest wysoka elektryczna przewodność właściwa oraz wysokie właściwości wytrzymałościowe. Obecnie obserwuje się w świecie wzrastającą tendencję do stosowania nowych stopów miedzi. W tej grupie materiałów szczególne znaczenie odgrywają stopy cechujące się ultradrobnoziarnistą strukturą osnowy. W pracy badano właściwości mechaniczne oraz mikrostrukturę utwardzanych wydzieleniowo stopów miedzi odkształcanych metodą cyklicznego przeginania i prostowania. Badaniu poddano taśmy ze stopów miedzi CuCr0.6 and CuNi2Si1 o grubości 0,8 mm wyżarzanych w 650°C przez 1 godzinę. Cykliczne przeginanie i prostowanie zrealizowano na skonstruowanym do tego celu stanowisku zainstalowanym na maszynie wytrzymałościowej. Badaniu poddano zmiany właściwości mechanicznych taśmy (twardość HV, wytrzymałość na rozciąganie, umowna granica plastyczności), jak również zmiany mikrostruktury w zależności od ilości cykli deformacji. Badania mikrostruktur prowadzono za pomocą mikroskopii świetlnej i elektronowej (TEM i SEM wyposażony w EBSD)

Proces cyklicznego przeginania i prostowania efektywnie zmniejszał wielkość ziaren taśm ze stopów CuCr0.6 CuNi2Si1, rokując dobre nadzieje jako metoda do otrzymywania struktury ultradrobnoziarnistej w płaskich wyrobach walcowanych.

## 1. Introduction

A growing trend to use precipitation strengthened copper alloys is recently observed world-wide. Within this group of materials particular attention is drawn to those with ultrafine grain size (UFG) of a copper matrix, which exhibit higher mechanical properties than the microcrystalline copper alloys.

To produce bulk copper materials of the ultrafine grain sizes the following methods are applied: powder metallurgy technique [1-6], severe plastic deformation methods, mainly equal–channel angular pressing (ECAP) [7-11], high-pressure torsion (HPT) [12-14] and hydrostatic extrusion (HE) [15]. These methods do not proceed continuously, and they seem to be impractical for manufacturing of flat, ultrafine grained materials. Recently a new technique, repetitive corrugation and straightening (RCS) [16-18], were developed for production of UFG microstructures in flat products. In the continous repetitive corrugation and straightening (CRCS)

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process (Fig. 1), a work-piece is repetitively corrugated and straightened without any significant change in the cross-section and what is very important, this process can be easily adapted to large-scale production.

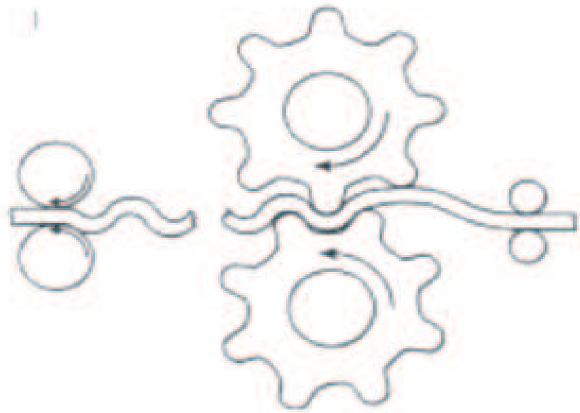


Fig. 1. Scheme of continuous RCS method [17]

The main objective of this work was to study the changes of the mechanical properties as well as the microstructure evolution versus cycle number of deformation of the CuNiSi and CuCr strips processed with the CRCS method.

## 2. Experimental procedure

Investigated material was precipitation hardened copper alloy with addition of:

– 2%Ni and 1% Si (CuNiSi),

– 0,6%Cr (CuCr)

prepared by melting and alloying in an open-air induction furnace, followed by casting into 130x170 mm mould. Ingots were hot rolled down to strip thickness of 3 mm. After brush cleaning of surface, the strips were cold rolled down to thickness of 0.8 mm. Strip samples 1000 mm in length and 20 mm in width were annealed at 650°C for 1 hour, and then prepared for tests.

Continuous repetitive corrugation and straightening process was conducted by strip drawing through toothed rolls (corrugation) and plain rolls (straightening) set. All rolls were assembled in die set giving possibility to control the rolling gap. The set was installed on INSTRON tensile testing machine, giving possibility of strip deformation (true strain about 0.8 in one pass). The investigated strips were immovably fixed during test and the set of rollers was shifted with movement of cross-bar of the tensile test machine. Process was conducted reversibly. 6, 12, 24 or 34 cycles of continuous repetitive corrugation and straightening were carried out. Thickness of the strips after the process was reduced to 0.7 mm. Microstructure studies were carried out on the samples of the initial material and the one after 34 cycles using optical and electron (SEM, TEM) microscopy. Transmission electron microscope investigations were performed at JEOL JEM 2000 FX. Observations were made on thin foil parallel to the strip surface. Crystallographic orientation analysis was done using electron backscattered diffraction (EBSD) setup on Philips SEM. The scanning parameters were set in such way that a grain boundary was defined when the disorientation between adjacent measurement points was higher than 6°. As the result the grain size determined by EBSD was smaller than the actual value. To ensure precision, these results were used in combination with TEM to determine the correct value. The mechanical properties of strips after 6, 12, 24 and 34 cycles were investigated in tension tests on INSTRON tensile testing machine.

## 3. Results and discussion

### 3.1. Microstructure

There were no significant changes in microstructure observed with optical microscopy before and after CRCS process for both alloys. It could be said, that after last annealing without any mid-process precipitation the microstructure of the particles correspond to their equilibrium BCC structure. Analysis with SEM equipped in electron back-scattered diffraction system provides possibility for precise identification of crystal structure of the studied materials (Orientation Imaging Metallography, OIM). Microstructure refinement was observed after CRCS process for the CuNiSi alloy strip (Fig. 2 and 3) and for CuCr alloy strip (Fig. 4 and 5). Cross-section of grains in initial strips did not exceed 150 $\mu m^2$ for CuNiSi and 170 $\mu m^2$ for CuCr alloys. In most cases area of the grains cross section was below 60 $\mu m^2$ for the CuNiSi and below 120 $\mu m^2$ for CuCr alloys. We can see on the histograms that before deformation most of the grain boundaries had large disorientation angle (over 60°). After CRCS process, number of grain boundaries with smaller angle increased, also with disorientation angle under 10°. The grain size determined by EBSD measurements seems to be smaller than the actual value. To ensure precision, these results were compared with TEM studies results to determine the correct value. Figures 6a and 6b show TEM micrographs of initial and deformed (34 passes) microstructure of the CuNiSi alloy. Figures 6c and 6d show TEM micrographs of initial and deformed (34 passes) microstructure of the CuCr alloy. In both cases the individual grains or subgrains were produced inside the primary grains whose sizes were ranging from about 100 nm to a few hundred nanometers. Also, many dislocation cells and arrays of dislocations were observed.

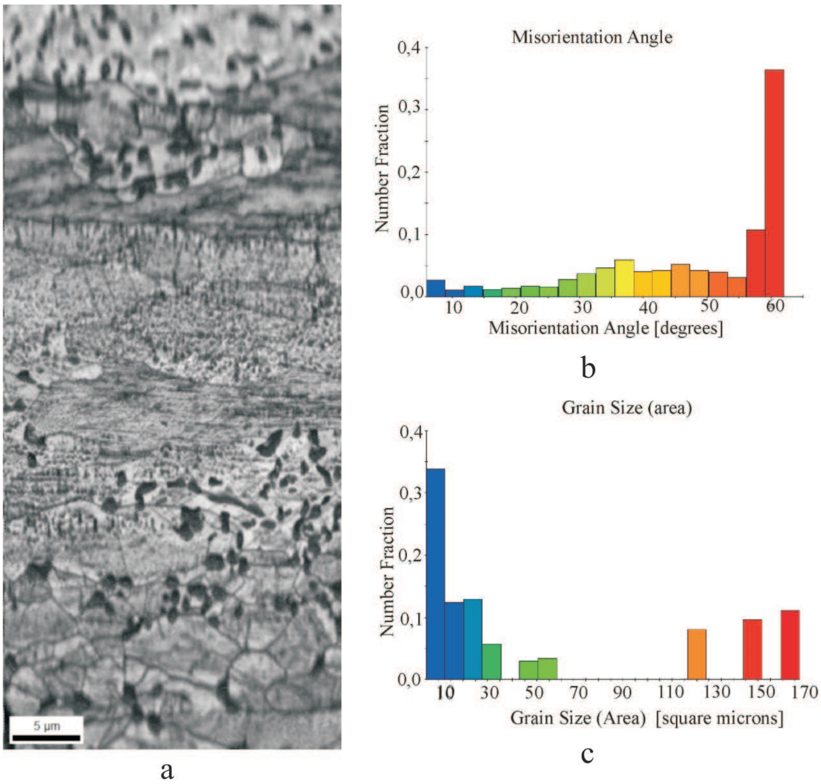



Fig. 2. Microstructure of CuNiSi alloy strip as annealed (a), with grain boundaries disorientation (b) and grain size distribution (c), SEM with EBSD

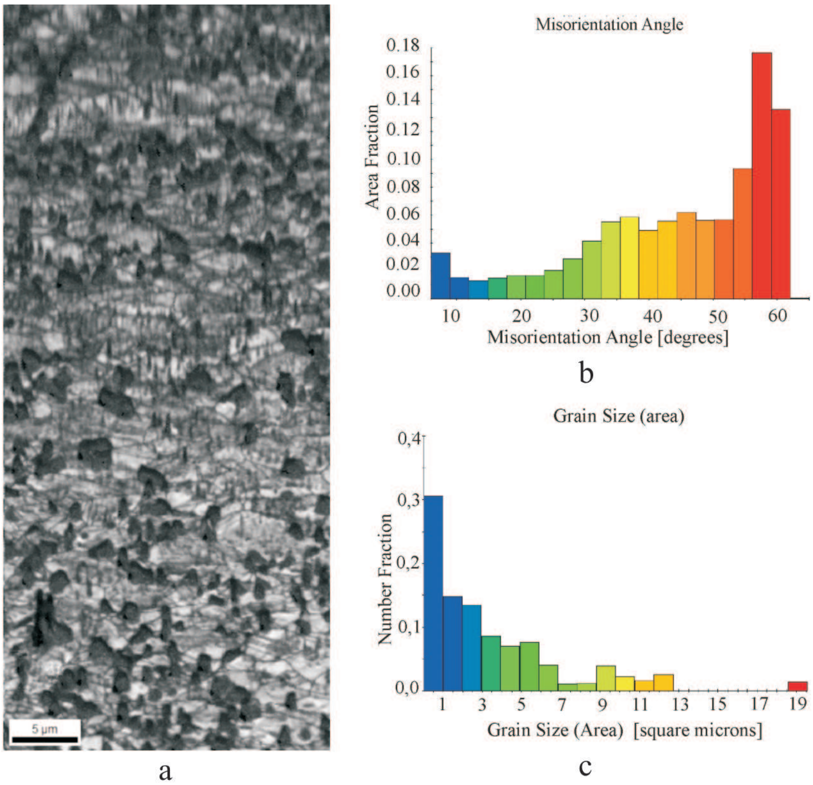



Fig. 3. Microstructure of CuNiSi alloy strip after 34 passes of deformation (a), with grain boundaries disorientation (b) and grain size distribution (c), SEM with EBSD

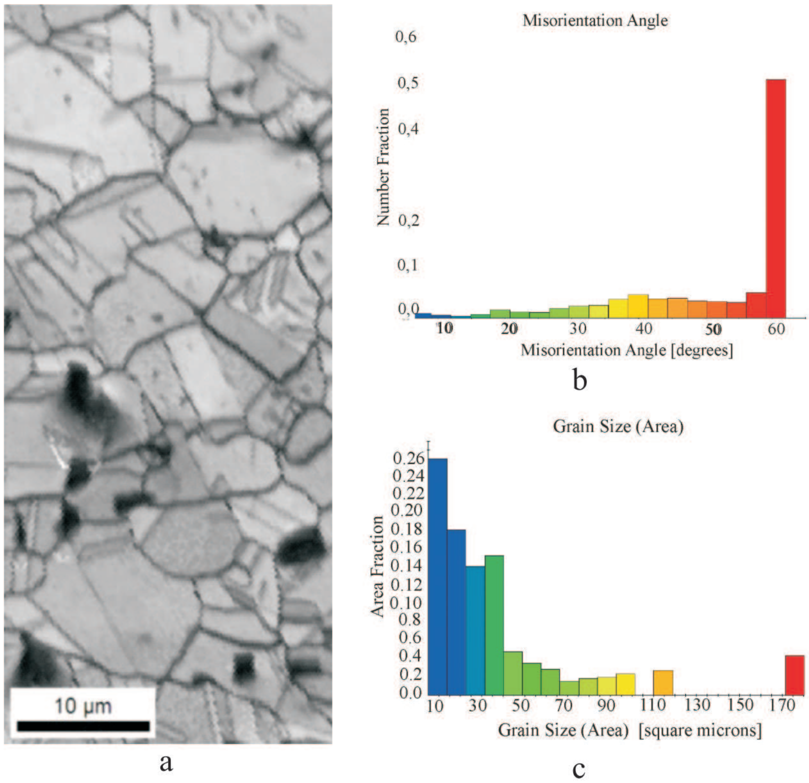



Fig. 4. Microstructure of CuCr alloy strip as annealed (a), with grain boundaries disorientation (b) and grain size distribution (c), SEM with EBSD

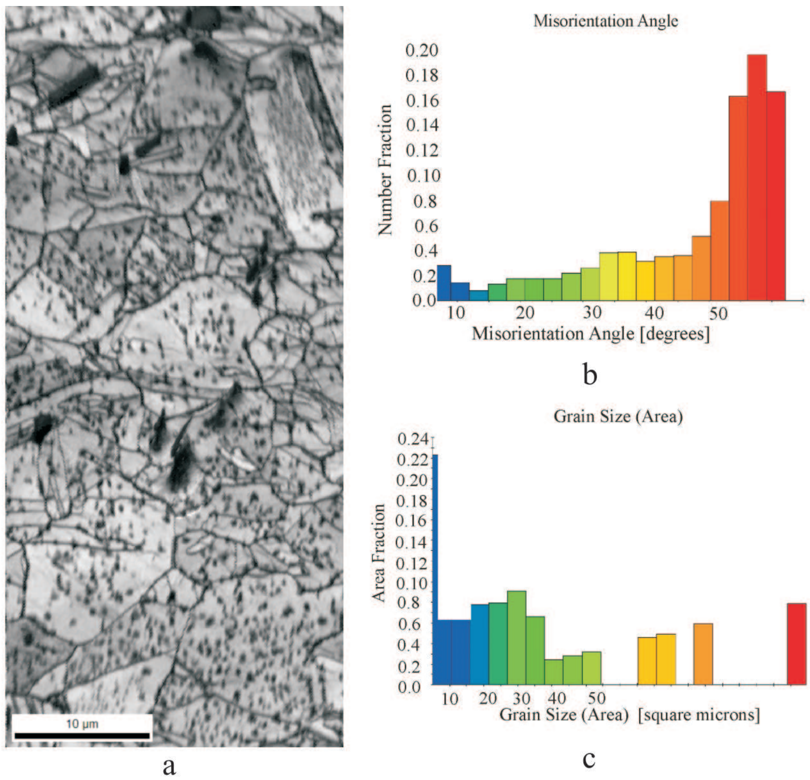
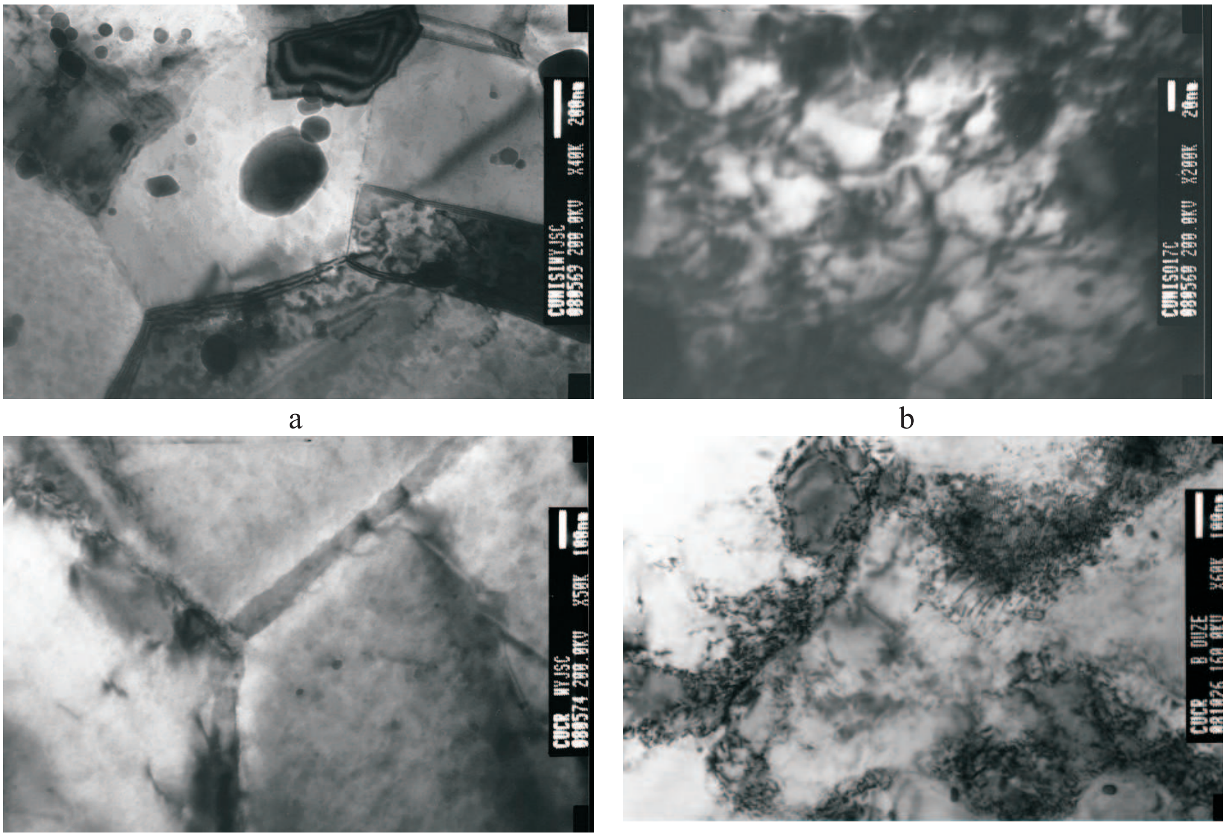



Fig. 5. Microstructure of CuCr alloy strip after 34 passes of deformation (a), with grain boundaries disorientation (b) and grain size distribution (c), SEM with EBSD




a b c d

Fig. 6. Microstructure of CuNiSi alloy strips: as annealed (a), after 34 passes of deformation (b); and CuCr alloy strips: as annealed (c), after 34 passes of deformation (d); TEM

### 3.2. Mechanical properties

The study of the mechanical properties (tensile and hardness tests) were conducted on CRCS samples that were annealed at 650°C for 1 h before corrugation and straightening. These results versus number of deformation passes are shown in Fig. 7.

The initial CuNiSi and CuCr sample showed large ductility. Work hardening in the CRCS process caused a large decrease in ductility of the sample and increase of strength.

The strength characteristics of CuNiSi strip such as yield strength and ultimate tensile strength increased by a factor 1.4 and 1.1 respectively. Maximal strengthening effect was achieved after 24 cycles of CRCS process. Further deformation caused decreasing of the strengthening factors to the values of about 1,2 and 1,1, because UTS decreased after 34 deformation cycles.

The ductility of the samples expressed by relative elongation decreased from 26% to about 5% after 24 passes, then it became stable.

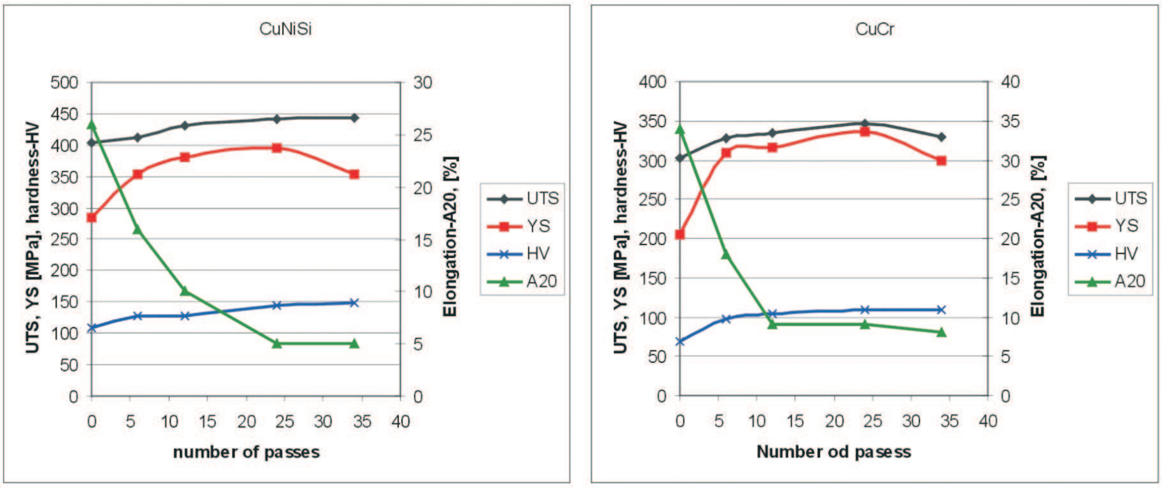
Microhardness of the strip increased from about 100 to about 150 HV.

The similar strength characteristics for the CuCr strip increased by a factor of 1.7 and 1.2 respectively. Maximal strengthening effect was achieved after 24 cycles of CRCS process. Further deformation caused decreasing of the strengthening factors to the values of about 1.5 and 1.1.

The ductility of the samples expressed by the relative elongation decreased from 34% to about 8% after 12 passes, then it became stable or decreased slowly.

Microhardness of the strip increased from about 70 to about 110 HV.

These results indicated complex deformation pattern and possibility to activate new slip systems, thus lowering the deformation resistance during CRCS deformation.




a b

Fig. 7. Changes of mechanical properties of CuNiSi (a) and CuCr (b) strip during CRCS processing

### 3.3. Theoretical calculation of yield strength value

Theoretical calculations of yield strength value for investigated material were carried out for development of properties and technological process [19-21].

$$\sigma_{0,2} = \sigma_0 + \sigma_{SS} + \sigma_{HP} + \sigma_{OR} \tag{1}$$

where:

$\sigma_0$ – Peierls stress (neglible in fcc materiale)

$\sigma_{SS}$ – stress caused by solid solution (neglible for annealed materials where alloying elements are present in precipitated particles)

$\sigma_{HP}$ – stress caused by graine structure according to the Hall-Petch's formula

$\sigma_{OR}$ – stress caused by presence of hard particles in the matrix according to the Orowan's formula.

In this case increase of the yield strength of processed alloys is caused by metal matrix grain refinement ($\sigma_{HP}$) and presence of precipitated particles ($\sigma_{OR}$) according to the Hall-Petch and Orowan formulas (2) and (3).

$$\sigma_{HP} = k_{HP} d^{-1/2} \tag{2}$$

where:

$k_{HP}$ – Hall-Petch's equation coefficient assumed 4,5 MPa mm $^{1/2}$

d – in matrix grain diameter, assumed 10μm for annealed CuCr, 500 nm for RCS processed CuCr, 1 μm for annealed CuNiSi and 300 nm for RCS processed CuNiSi

$$\sigma_{OR} = 0,9M \frac{[\ln(8r_s/b)]^{3/2}}{[\ln(L/b)]^{1/2}} \left[ \frac{K^{edge}}{b(L-2r_s)} \right] \tag{3}$$

$$r_s = \frac{\pi}{4} r_{cz}, \quad K^{edge} = \frac{Gb^2}{4\pi(1-\nu)}, \quad L = \sqrt{\frac{32}{3\pi f}} r_s \tag{4}$$

where:

M –Taylor's factor, assumed 2,45

b –Burger's vector, assumed 0,256 nm

$K^{edge}$ – pre-logarithmic line tension factor

L – mean planar dispersoid spacing

$r_{cz}$ – mean radius of the particles, assumed 6nm for CuCr and 30 nm for CuNiSi

G – shear modulus, assumed 42000 MPa

$\nu$ – Poisson's ratio assumed 0,3

f – volume fraction of dispersoids, assumed 0,66% for CuCr and 4% for CuNiSi

Calculation results of yield strength value have been compared to the values obtained in experiment in Figures 8 and 9.

Calculation results are comparable with experimental data. Comparing influence of Hall-Petch and Orowan mechanism on strengthening of studied alloys we can see that in initial state (coarse grains) both mechanisms play similar role in strengthening. After CRCS processing grain refinement is main mechanism of strengthening for both alloys. There is no scientific data concerning studies of grain refinement effect in precipitation strengthened copper alloys. Simultaneous effect of grain size refinement and second phase particles of copper based materials obtained by powder metallurgy methods were studied in papers [1-6,20]. The mechanism of deformation of materials fabricated by powder metallurgy technique strongly depends on material porosity and slip on conglomerates boundaries. The relationship between volume fraction, size of strengthening particles and matrix grains is likewise essential. The volume fraction of strengthening particles cannot exceed a maximum value at which the material brittleness is observed.

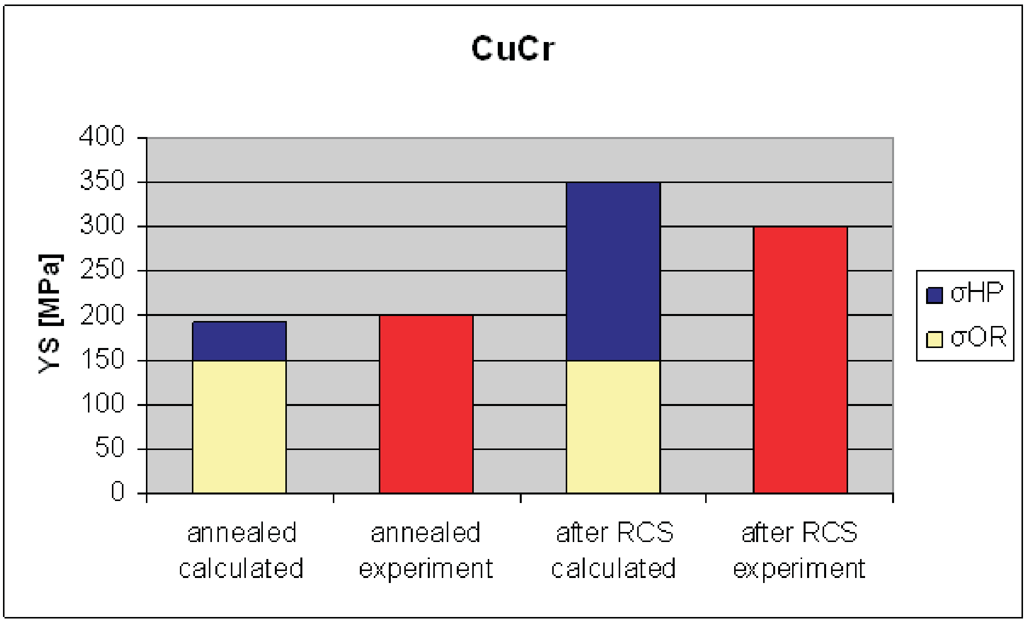



Fig. 8. Comparison of yield strength value calculated and obtained in experiment for CuCr alloy

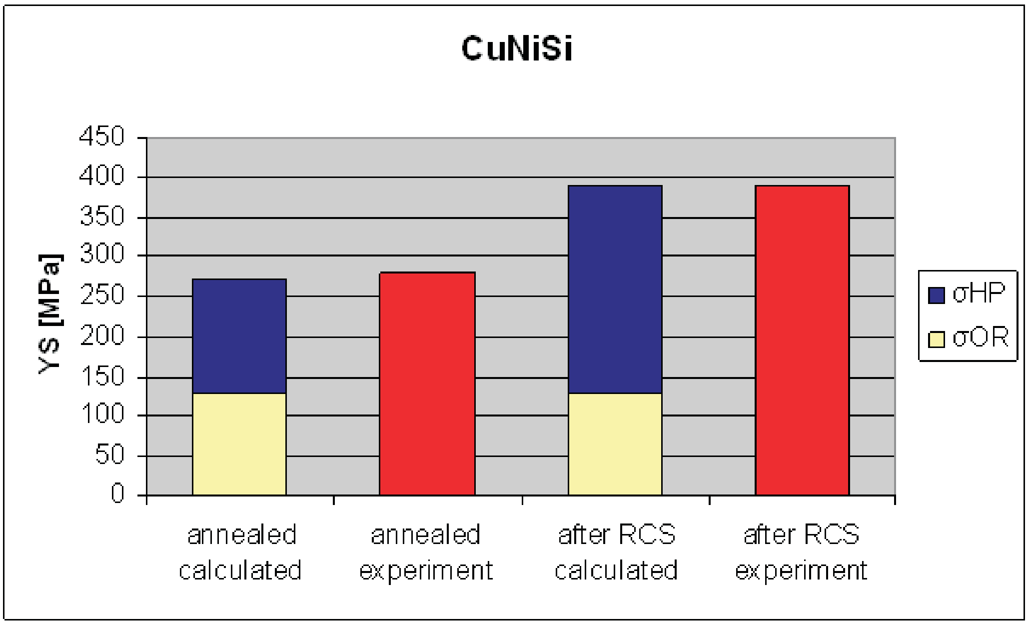



Fig. 9. Comparison of yield strength value calculated and obtained in experiment for CuNiSi alloy

Thus the results of investigation of materials obtained by means of powder metallurgy and precipitation strengthened alloys cannot be directly compared.

## 4. Conclusions

The study aimed to investigate mechanical properties and microstructure of CuNiSi and CuCr alloy strips produced during continuous repetitive corrugation and straightening (CRCS). Based on the obtained results, the following conclusions can be drawn:

- The CRCS process effectively reduced the grain size of the studied strips, demonstrating the CRCS as a promising new method for producing ultra fine grained metallic strips.
- The OIM analysis of microstructure after CRCS (34 passes) revealed refinement of average grain size (determined by their cross section).

- The dimensions of structure elements revealed by OIM analysis were larger than those determined by TEM. TEM micrographs of the deformed microstructure showed that the individual grains or subgrains were produced inside the primary grains. Their sizes were in the range from about 100 nm to a few hundred nanometers. Also many dislocation cells and arrays were observed.
- The strength characteristics of the investigated strips such as yield strength and ultimate tensile strength increased after CRCS in relation to initial state and remained virtually constant in the deformation range of 12-24 cycles. Further increase of deformation caused decrease of strength.
- Comparing influence of Hall-Petch and Orowan mechanisms on strengthening of studied alloys we can see that in initial state (coarse grains) both mechanisms play similar role in strengthening. After CRCS processing grain refinement is the main mechanism of strengthening for both alloys.

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