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EFFECT OF THE COMBINED HEAT TREATMENT AND SEVERE PLASTC DEFORMATION ON THE MICROSTRUCTURE OF CuNiSi ALLOY

The aim of this work was to study the microstructure and functional properties of CuNi2Si1 alloy. The material was prepared classically by melting, casting, hot rolling and cold rolling. The obtained strips were processed with combined operations of supersaturation, ageing and one of the intensive deformation method – repetitive corrugation and straightening. The efficiency of RCS operation in shaping of functional properties in precipitation hardened copper alloys depends not only on tool geometry and operating parameters but also on whether and at what stage of strip production the supersaturation operation was applied. Application of the supersaturation before RCS operation broadens the potential to shape the set of functional properties. Comparable functional properties of the precipitation hardened copper alloy strips can be reached without application of the supersaturation operation in their manufacturing processes. The process of RCS applied after annealing, and the potentially slightly lower mechanical properties would be compensated by higher electrical conductivity.

Keywords: Copper Alloy, Precipitation Hardening, Microstructure, Mechanical Properties; Electrical Properties

1. Introduction

Miniaturization of electronic and electrical components as well as the rising costs of materials are the driving force for development of high-quality copper alloys which are used in the automotive, railway, electrical engineering and ICT industries. Miniaturization requires particularly high mechanical properties, and at the same time medium or high electrical conductivity is also required. Components used in such applications often have to show stability of these properties in a temperature range from -40°C to 180°C, also under load, and also often resistance to stress relaxation and fatigue resistance.

Precipitation hardened copper alloys, including alloys of Cu-Ni-Si type, are broadly used in the above applications, especially in openwork paths or resilient electrically conducting components. Thanks to concentration of alloying additions in small precipitates during ageing process the copper matrix remains relatively free from atoms of impurities and atoms of alloying elements, which in turn makes combination of high strength and high (electrical or thermal) conductivity in the copper alloys possible. Corson [1] was the first to describe the mechanism of precipitation of Ni-Si particles in Cu-Ni-Si alloys. Currently produced, standardized alloys, such as C7025 or C7035, contain about 3% of Ni_2Si phase particles. For such content of Ni_2Si phase the temperature of supersaturation can be assumed close to 900°C.

The high strength (up to 800-900 MPa) can be reached after ageing and cold-deformation of supersaturated alloys or by supersaturation, cold-deformation and then ageing. Structurally, this corresponds to the state in which highly dispersed precipitates (either coherent or partially coherent) of Ni2Si phase of less than 20 nm diameter are present in a copper matrix [2]. The hardness peak is reached after ageing in the temperature range of 400-500°C.

The study included work [3] indicated, that optimum combination of hardness (HV = 150) and electrical conductivity (γ = 22 MS/m) have been obtained for CuNi2Si1 alloy strips ofter solution treatment and ageing at 550°C temperature in time 120 min. An intensive precipitation processes of nonmetric, coherent particles of Ni_2Si phase have been during ageing. This process proceeded homogeneously in the matrix at temperature range 267-381°C.

Satisfactory properties of CuNiSi alloys used in electrical connectors aroused interest in these alloys in the early 90s [4-6]. Up till now studies have been focused on problems of understanding and optimization of processes for preparation of ternary Cu-Ni-Si alloys of chemical composition between CuNi2Si1 and CuNi3Si1 and more complex alloys, typically containing cobalt, chromium, often with a small addition of magnesium. Magnesium atoms improve resistance to stress relaxation in the result of solution strengthening ($r_{Mg} - r_{Cu} / r_{Cu}$ = 25%). They also affect the mechanism of Ni_2Si phase formation.

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Chromium precipitates in the form of coherent strengthening particles during alloy ageing and increases its strength. The disadvantage of chromium addition is the tendency to form very hard particles of high-temperature Cr_3Si phase that reduce life of tools due to increased friction.

Wider possibilities for reaching preferred mechanical properties and electric conductivity can be achieved in these alloys by application of technologies of cold deformation and in combination with different variants of supersaturation and ageing processes [7-12]. In recent years, processes that use strong and complex plastic deformation (i.e. SPD – severe plastic deformation) are becoming widely used in manufacturing [2,10-12]. These processes are widely used in production of components of pure copper and solution strengthened copper but there are not much studies of fabrication of components from precipitation hardened copper alloys. In particular, there is not much information on development of a set of mechanical and electrical properties in technological processes with SPD techniques, which reduce the grain/subgrain down to ultrafine or nano-metric size, thereby changing both the mechanism and kinetics of the aging process, and, consequently, the strengthening mechanism.

In the earlier works of the authors [13] the base material was in a form of strips made of Cu, CuZn36, CuSn6. Cold deformed strip samples were annealed in temperature of 550°C for 1 hour in an electric resistance furnace. The annealed strips were subjected to repetitive corrugation and straightening.

After the RCS process the yield strength and tensile strength increased as compared to the annealed state. The effect of strengthening of strips from CuZn36 and CuSn6 alloys from in RCS process was higher than in the process of strengthening of these alloys in a classical rolling process. Elongation of all tested samples after RCS process was in the range of 4.3 to 7.2%.

Low temperature annealing of strips (200°C/1h) resulted in stabilization of the achieved in the RCS process properties of the strips, which retained their mechanical properties (tensile strength, yield strength) similar to those obtained in the RCS process. Elongation and hardness did not change.

In this study, it was decided to examine strips made of precipitation hardened CuNi2Si alloy. The processing of this material applies combination of the supersaturation and aging operations as well as deformation by RCS method.

2. Characteristics of material and methodology of studies

For the studies a ternary CuNi2Si1alloy was selected, which was used for production of strip of 0.8 mm thickness. The alloy was produced by the classical method of melting in an open induction furnace. Then the ingots of cross-section 35×120 mm were hot rolled to the thickness of 3 mm, purified and further cold rolled down to the thickness of 0.8 mm. The produced material was cut into 0.8×20×1500 mm strips. Thus prepared strips were held at 900°C for 1 hour and then supersaturated in water. The supersaturated material was then used as a starting material for further studies.

The study was divided into four stages:

- supersaturation 900°C for 1 hour;
- supersaturation (900°C for 1 hour) + ageing (480°C for 2 hours);
- supersaturation (900°C for 1 hour) + ageing (480°C for 2 hours)+ SPD (RCS);
- supersaturation (900°C for 1 hour) + ageing (480°C for 2 hours)+ SPD (RCS) + ageing (450°C for 2 hours).

The samples were subjected to repetitive corrugation and straightening (RCS) process with a laboratory rolling mill as described in the study [13]. The samples were 10 times bent on toothed rolls and 10 times on groove rolls and then straightened on plain rolls. The process was 8 times repeated.

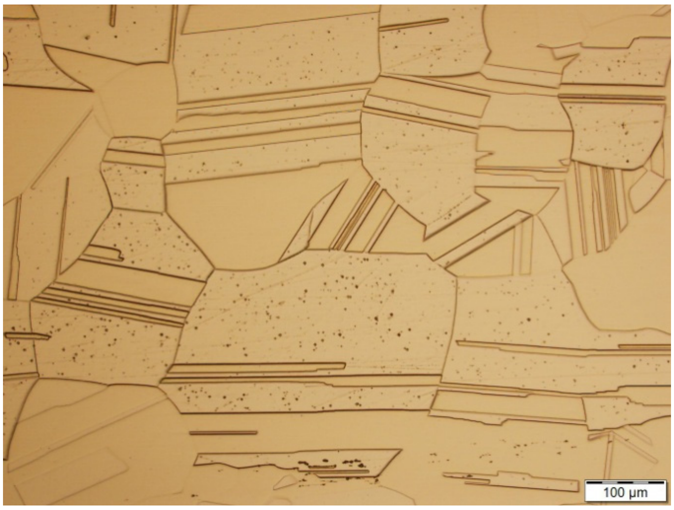
After each step the changes in microstructure were analyzed, in particular by examination with optical, scanning electron microscope, EBSD technique and transmission electron microscopy. These techniques provided possibilities to observe changes in the microstructure of the alloy in the manufacturing process and explain the possible impact of SPD operations on the properties of semi-finished or finished components. Additionally, after each step conductivity and hardness were measured.

3. Results of studies

Microstructure of supersaturated strips was typical of copper alloys in recrystallized state, a number of twin boundaries were observed. Images of microstructure on the sections transverse to the rolling direction were similar to the microstructure observed on longitudinal sections, and in both cases the grain diameter usually exceeded 100 μm (Fig. 1). Presence of individual dislocations in the samples after supersaturation was revealed in the studies with application of scanning electron microscopy. Their amount, as seen in a form of etch figures on the surface of a sample in the examinations by scanning microscope, is typical of the properly annealed material (Fig. 1B). The average particle size, as estimated by EBSD technique, is fairly uniform and close to the value of 100 μm, while distribution of misorientation angles of grain boundaries are typical of recrystallized structure. High-angle boundaries (above 15°) dominate.

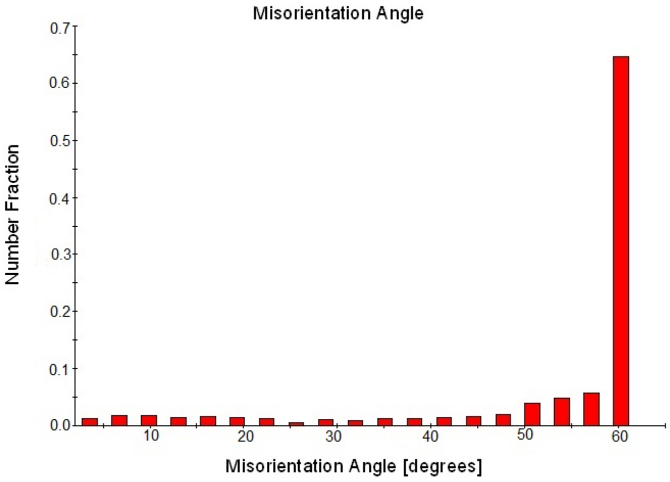
The presented results of examination of microstructure of the aged sample after supersaturation show that there is no clear grain growth in this process, while the nucleation processes are observed (Fig. 2). Just like in the samples after supersaturation the distributions of misorientation angles of grain boundaries are typical of the recrystallized structure. High-angle boundaries (above 15°) dominate. The average grain size, estimated by EBSD technique, is quite uniform and slightly increased as a result of ageing to approx. 115 μm.

In the microstructure after the RCS process slip bands were clearly observed. The complex deformation state in the tests resulted in double slip systems in all grains (Fig. 3). In the samples after heat treatment and deformation the maximum grain diameter was less than 245 μm, and the smallest was 8.6 μm. The average grain size, estimated by EBSD technique, is about



a) Optical microscope

b) EBSD

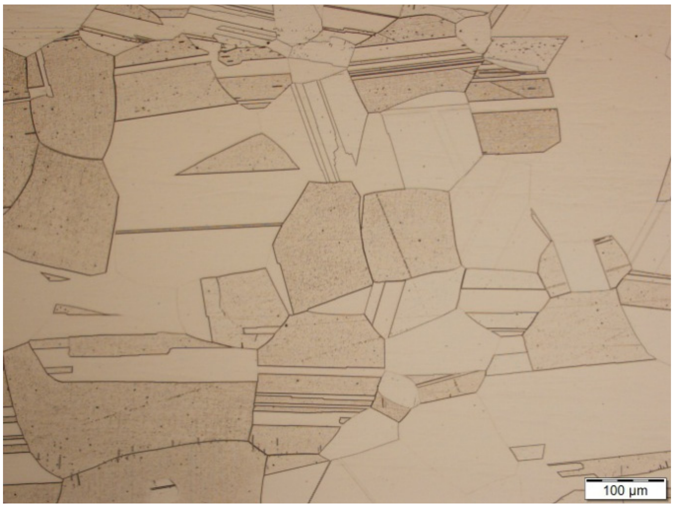


c) distribution of grain misorientation

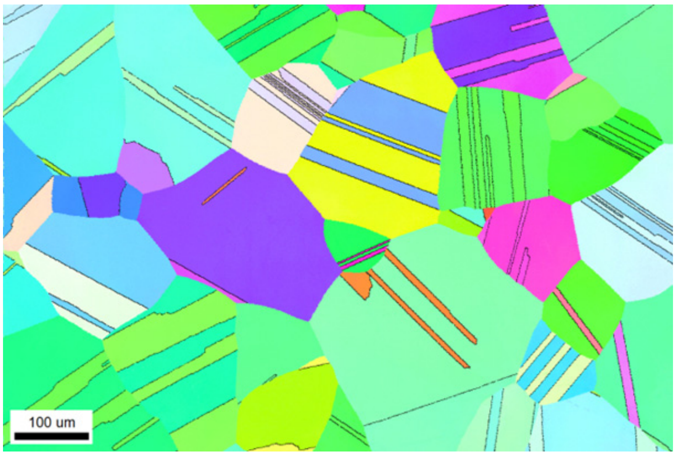
Fig. 1. Microstructure of CuNi2Si1 alloy samples after supersaturation at 900°C for 1 hour, perpendicular metallographic section

125 µm. The distribution of misorientation angles of grain boundaries is typical of the recrystallized structure. Low-angle boundaries (below 15°) dominate.

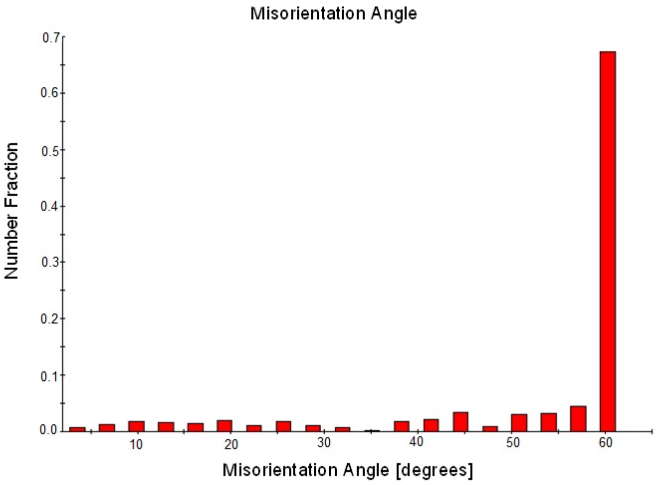
The effects of deformation were also observed in the material after additional ageing (Fig. 4). The process of additional



a) Optical microscope



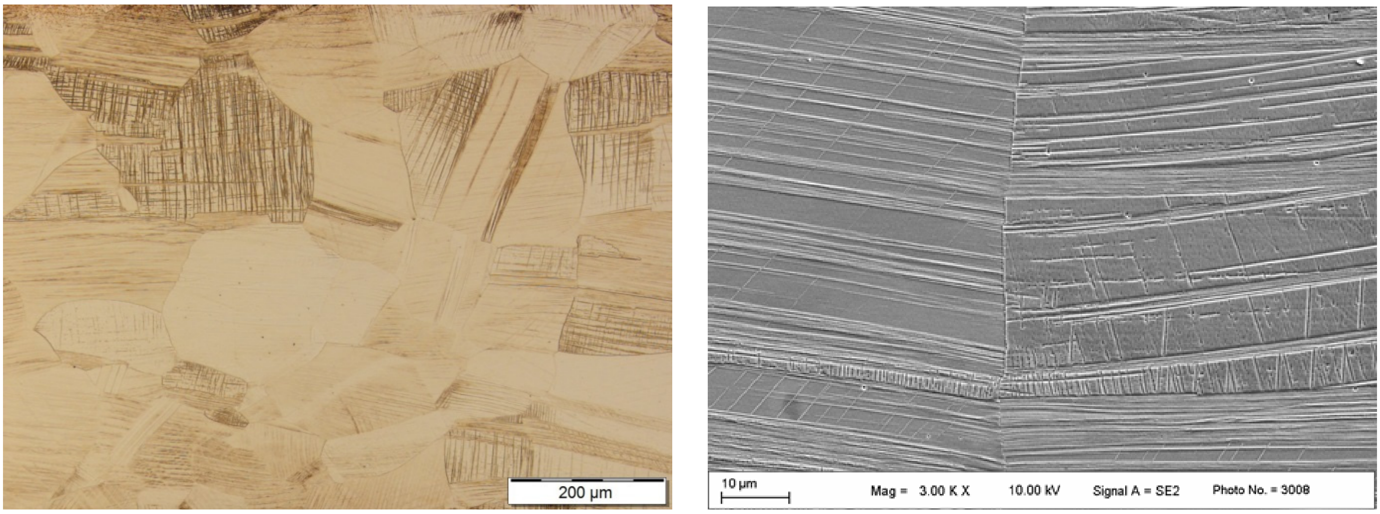
b) EBSD



c) distribution of grain misorientation

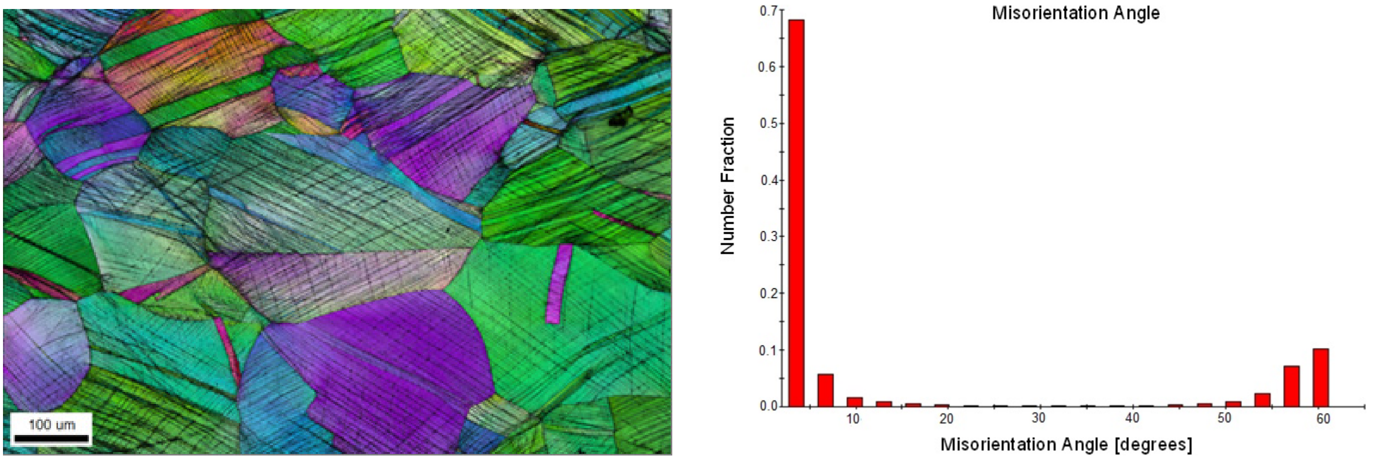
Fig. 2. Microstructure of CuNi2Si1 alloy samples after supersaturation at 900°C for 1 hour and ageing (480°C for 2 hours), perpendicular metallographic section, etched section

ageing of the samples after previous heat treatment and RCS did not bring significant changes, neither in grain size nor in the distribution of misorientation angles of grain boundaries, when compared to the samples without additional ageing. The aver-



a) Optical microscope

b) SEM



c) EBSD

d) distribution of grain misorientation

Fig. 3. Microstructure of CuNi2Si1 alloy samples after supersaturation at 900°C for 1 hour, ageing (480°C for 2 hours), and RCS, perpendicular metallographic section, etched section

age grain size, estimated by EBSD technique, is about 125 µm. Low-angle boundaries (below 15°) dominate.

The complete supersaturation of the sample is confirmed by the results of examinations with application of transmission electron microscopy. In these studies, no undissolved in the process particles of Ni_2Si phase were observed. Presence of single dislocations was observed in the studies with application of scanning electron microscopy, while the observed density of dislocations, as seen in the studies with transmission electron microscope, might have been overstated by introduction of some additional strain in process of thin films preparation (Fig. 5).

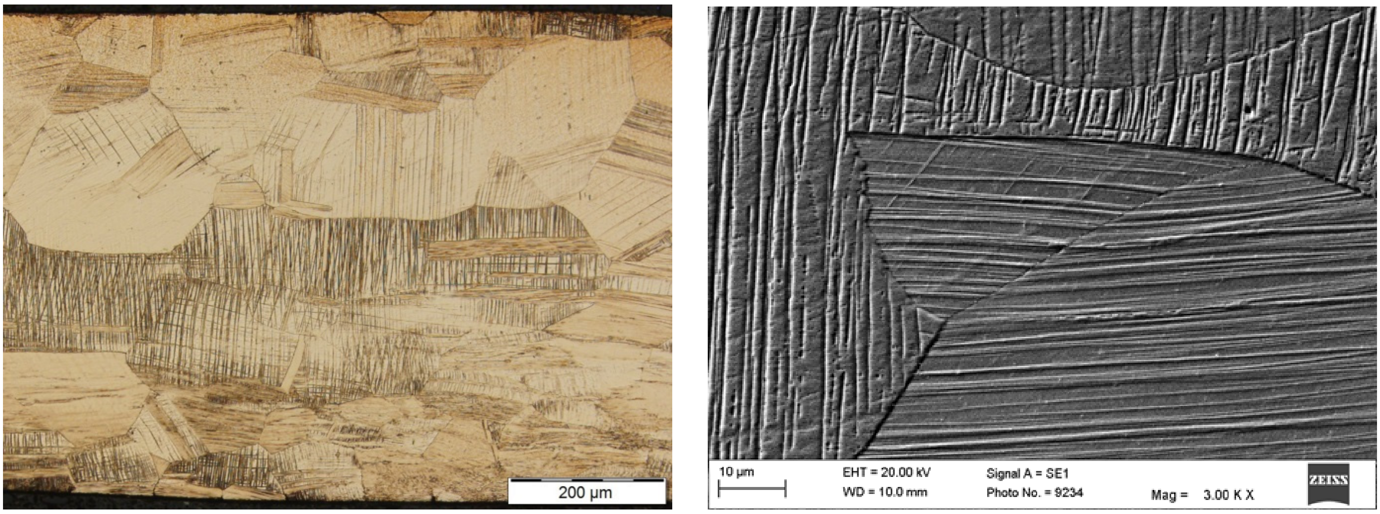
Vast majority of precipitates of Ni2Si phase in the aged sample is uniformly distributed in the alloy matrix (in the form of coherent particles having close to spherical shape), and the average size (average particle diameter) is in the range of 10-15 nm (Fig. 6). The second maximum, in the range of 30-50 nm, is associated with the process of heterogeneous nucleation of precipitates on dislocations. Furthermore, also larger particles of Ni2Si phase are observed, which nucleate in grain boundaries.

In the samples after heat treatment and RCS numerous instances of deflection of shear microbands after passing through the grain boundaries were observed, as well as presence of microbands that cause glide in the adjacent grain after reaching the grain boundary.

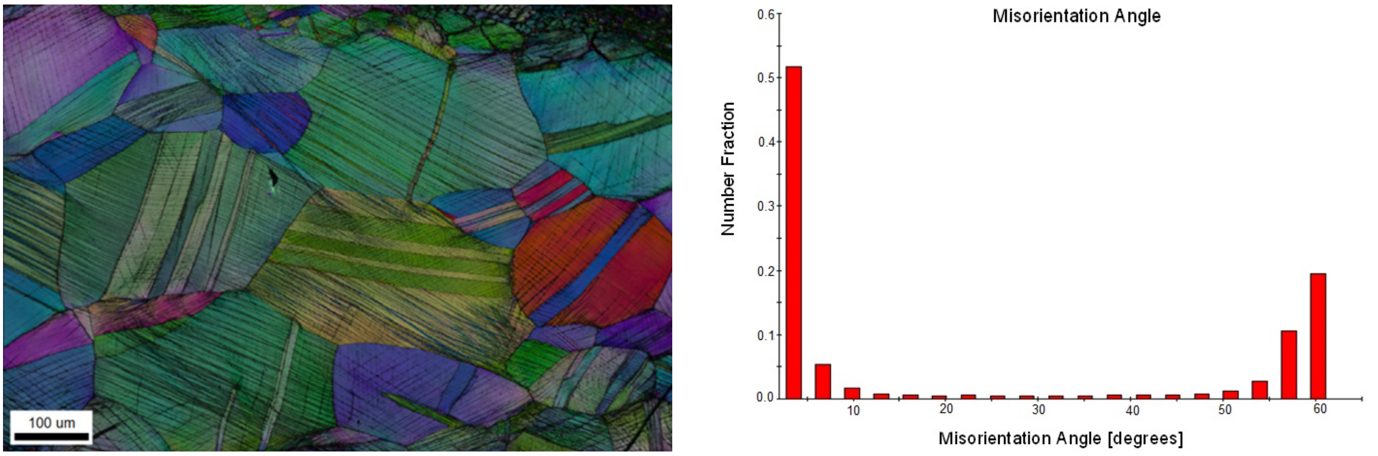
In the microstructure after heat treatment, RCS and additional ageing large particles of Ni_2Si phase were observed, nucleating in the grain boundaries or in the junctions where three grains come into contact of grain size at the level of a fraction of µm, and in the areas of intersection of shear bands (Fig. 8).

Observations with optical and scanning electron microscopes were conducted to examine evolution of the slip phenomenon, while the studies with the transmission electron microscope were applied to examine development of microstructure, mainly the dislocation one.

It was established that the mechanism of deformation is not uniform. In the individual grains 1-3 slip systems dominate. This configuration is observed in a large number of grains. Frequently microbands are observed, i.e. areas having a thickness of

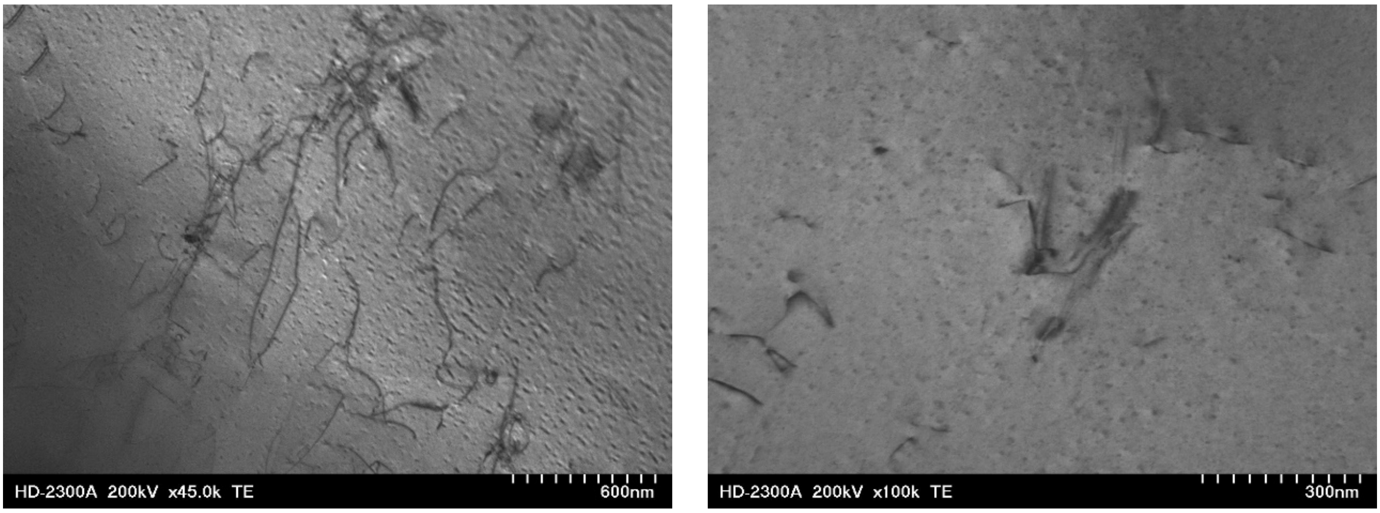


a) Optical microscope b) SEM



c) EBSD d) distribution of grain misorientation

Fig. 4. Microstructure of CuNi2Si1 alloy samples after supersaturation at 900°C for 1 hour, ageing (480°C for 2 hours), RCS and ageing (450°C for 2 hours), perpendicular metallographic section, etched section



a) Mag. 45.000× b) Mag. 100.000×

Fig. 5. Microstructure of CuNi2Si1 alloy samples after supersaturation at 900°C for 1 hour, TEM

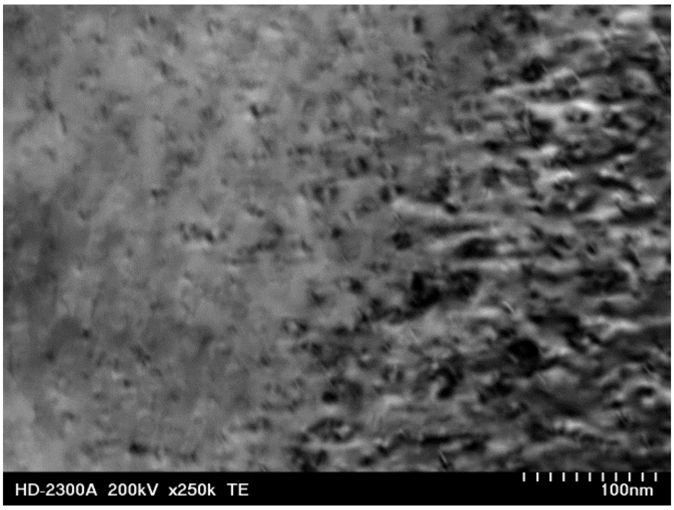
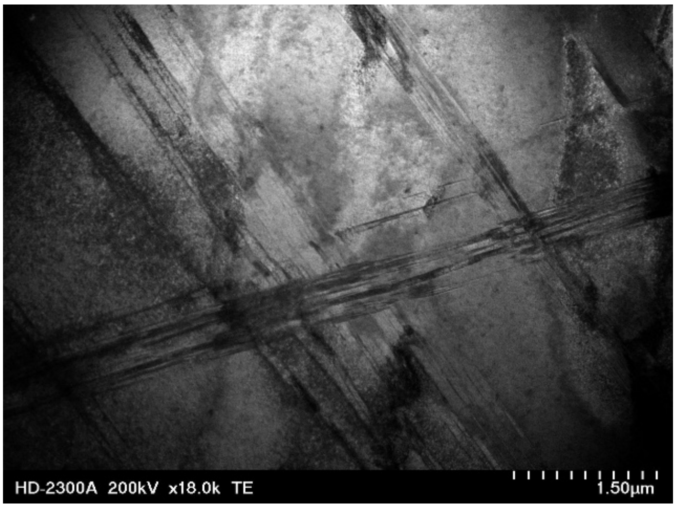
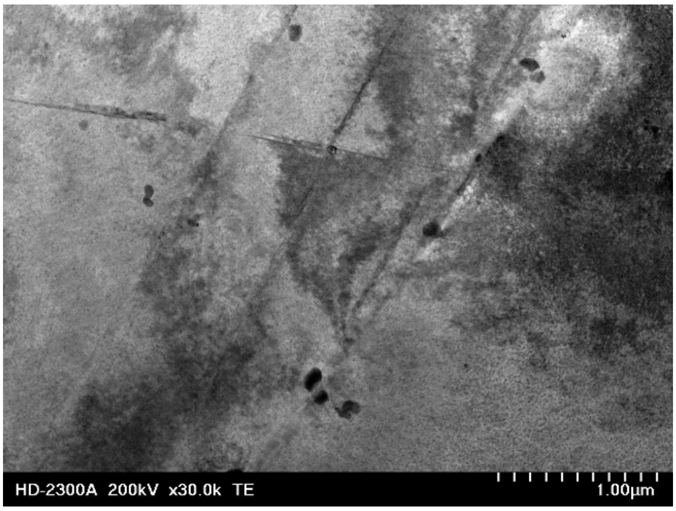


Fig. 6. Microstructure of CuNi2Si1 alloy samples after supersaturation at 900°C for 1 hour, ageing (480°C for 2 hours), TEM

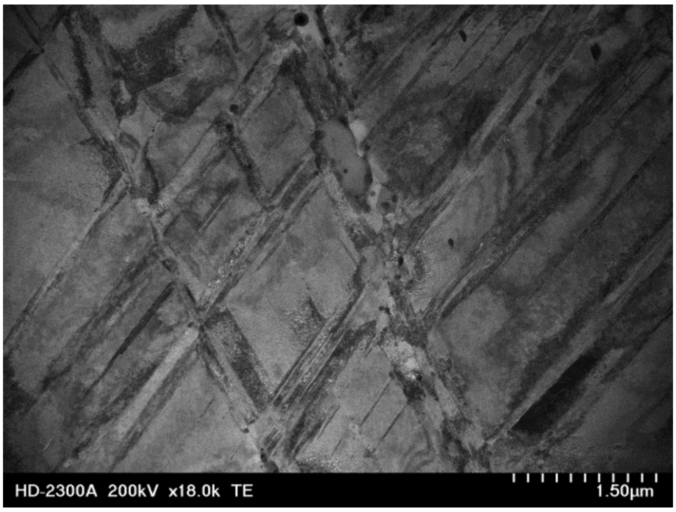


a) Mag. 18.000×

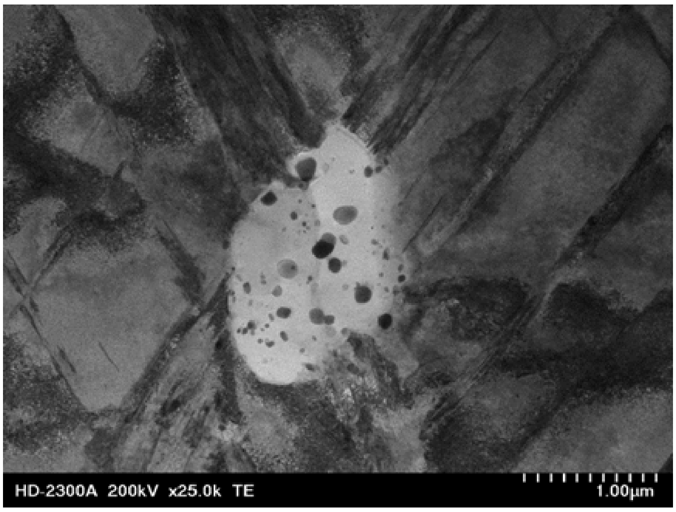


b) Mag. 30.000×

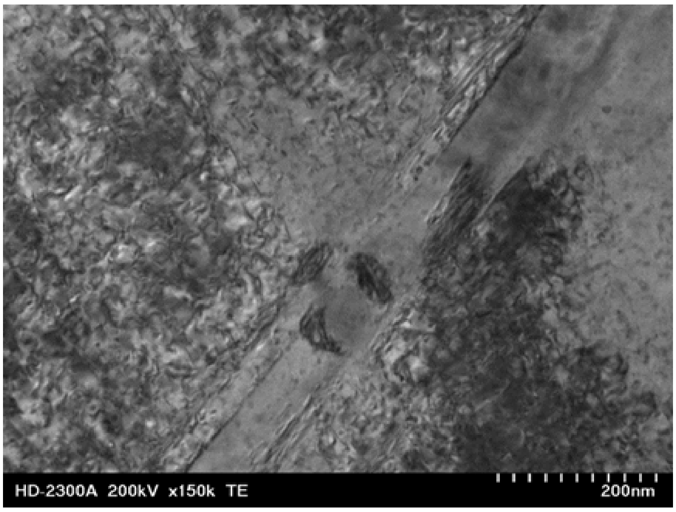
Fig. 7. Microstructure of CuNi2Si1 alloy samples after supersaturation at 900°C for 1 hour, ageing (480°C for 2 hours) and RCS; TEM



a) Mag. 18.000×



b) Mag. 25.000×



c) Mag. 150.000×

Fig. 8 Microstructure of CuNi2Si1 alloy samples after supersaturation at 900°C for 1 hour, ageing (480°C for 2 hours), RCS and ageing (450°C for 2 hours),TEM tenths of microns which carry very large non-dilatational strains within the individual grains only. In deformation of plastically heterogeneous material, the occurring gradient of deformation causes generation of long-range internal stresses. They are generated, for example, between adjacent, differently oriented grains in a polycrystal, at the interface, and also between two regions of different dislocation density, both in a single crystal and in a polycrystal. These are long-range stresses. Their accommodation takes place by generation of, so called, geometrically necessary dislocations. These are systems which provide compatibility of deformations between regions of plastically heterogeneous material, and the strains which correspond to that system can never exceed the local flow stress. In the initial stage of plastic deformation individual grains become deformed in a uniform way and usually one slip system dominates. With the increase of strain the misfit within the boundaries of the individual grains increases, which gives rise to stresses, and their accommodation takes place through generation of geometrically necessary dislocations. The largest misfit occurs within the grain boundaries, and that is why density of dislocations in this zone significantly increases when compared to the dislocation density inside the grains, causing additional long-range stresses. Therefore, the density of geometrically necessary dislocations is a characteristic feature of a given microstructure, depending mainly on the size and mutual arrangement of the grains and phases in the material.

4. Functional properties of CuNi2Si1 alloy

After each stage hardness HV and electrical conductivity γ of the samples were examined. The ageing process, in its early stages, is accompanied by increase of the measured hardness HV which is due to the interaction of small, coherent precipitates of Ni_2Si phase with dislocations. According to Orowan, the maximum increase of hardness and basic mechanical properties of the material is reached when the size of the particles, at their content of about 3%, is between ten and twenty nm. In the examined material which was aged after supersaturation hardness close to 185 HV was reached.

TABLE 1

Functional properties of examined samples

Property Sample	Hardness HV1	Electrical conductivity (γ), MS/m
supersaturation	70.5	6.84
supersaturation + ageing	183.5	8.35
supersaturation + ageing + SPD (RCS)	223.7	8.0
supersaturation + ageing + SPD (RCS) + ageing	208.3	8.43

In the sample in which in the final stage a complex process of deformation by RCS technique was applied after ageing a further, significant increase of hardness HV was reached. While the hardness HV of the sample after supersaturation and ageing was about 184 HV, in the sample after heat treatment and severe deformation the hardness increased to about 224 HV. It was observed that plastic deformation of the precipitation hardened polycrystalline material in the RCS process is a strongly heterogeneous process and the nature of this phenomenon has a localized character.

Application of additional annealing (ageing) after the RCS process reduces hardness of a sample. The hardness, however, remains at a significantly higher level than the hardness of the sample after supersaturation and heat treatment, while maintaining slightly more favorable electrical conductivity.

A comparison of the microstructures of samples after heat treatment and RCS and after heat treatment, RCS and additional ageing (especially in TEM) shows that reduction of hardness is caused by coagulation of precipitates of Ni2Si phase in the copper matrix, heterogeneous nucleation of that phase (mainly in the areas of intersection of the shear bands), and growth of the precipitates, as well as by starting of processes of recovery and/or recrystallization in microregions. The latter process was observed in microareas of intersecting shear bands mainly. In a large number of grains also more advanced stages of development of dislocation cell structure were observed.

While the electric conductivity of the examined alloy in a supersaturated state was about 6.8 MS/m, after ageing and supersaturation the conductivity increased to 8.35 MS/mm.

The process of ageing in its early stages is accompanied by increase of electrical conductivity. The scale of that increase depends on the degree of purification of a copper matrix from atoms of Ni and Si, reduction of concentration of vacancies in the copper matrix and on the dislocation density.

Electrical conductivity decreased with increasing number of cycles of deformation (rolling on toothed rolls, rolling on groove rolls – revolution × 10 times-straightening) (Fig. 9).

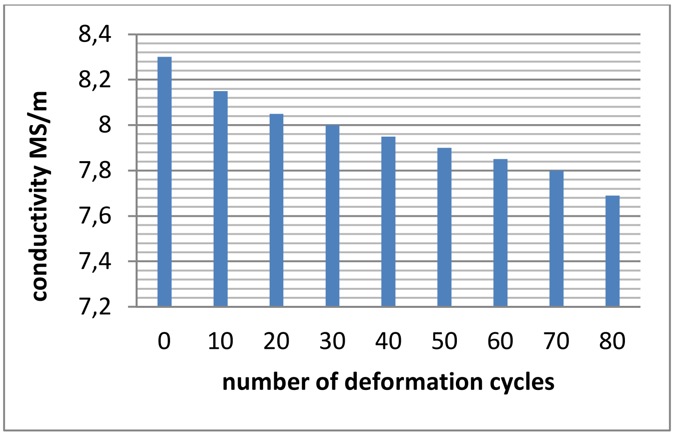


Fig. 9. Electric conductivity of CuNi2Si1 alloy after various stages of heat treatment and deformation

5. Conclusions

In summary, the following general conclusions can be drawn from the results of the studies conducted within the whole project:

- Application of cyclic operation of corrugation and straightening (RCS) in the manufacture of copper alloy strips makes it possible to reach a broader range of basic functional properties, i.e. mechanical properties (e.g. Rm, HV) and electrical conductivity. Increase of mechanical properties of single-phase alloys can be achieved by fragmentation of the microstructure (reduction of grain/subgrain size) or by increased dislocation density at small changes in electrical conductivity.
- Application of RCS operation provides possibility to control a wide range of changes in mechanical properties and electrical conductivity in the precipitation hardened copper alloys, by taking advantage of the influence of that operation on changes in the mechanism and kinetics of decomposition of supersaturated solid solution resulting directly from the growth of surface of the grain/subgrain boundary or from changes in the density and distribution of dislocations.
- The efficiency of RCS operation in shaping of functional properties in precipitation hardened copper alloys depends not only on tool geometry and operating parameters but also on whether and at what stage of strip production the supersaturation operation was applied. Application of the supersaturation before RCS operation broadens the potential to shape the set of functional properties.
- In production of strips the supersaturation is usually applied in the final operations and on small cross-sections. These are very troublesome operations and often impossible to be conducted in industrial environment (continuous process, high temperature, protective atmosphere and other onerous conditions).
- In the process of strip production with RCS and supersaturation operations it is most advantageous to apply the supersaturation directly before the RCS operation which is then followed by ageing. In such a case the supersaturation should be applied on thicker strips, and the final operations would be cold rolling and ageing.
- Comparable functional properties of the precipitation hardened copper alloy strips can be reached without application of the supersaturation operation in their manufacturing processes. The process of RCS could be applied after annealing, and the potentially slightly lower mechanical properties would be compensated by higher electrical conductivity.

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