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Z. RDZAWSKI*,**, J. STOBRAWA*,**, W. GŁUCHOWSKI*, J. SOBOTA*

MECHANISM AND KINETICS OF PRECIPITATION PROCESS IN SELECTED COPPER ALLOYS

MECHANIZM I KINETYKA WYDZIELENIA W WYBRANYCH STOPACH MIEDZI

The required functional characteristics expected from copper alloys have a major impact on the technological production process, therefore there is a strong need to acquire knowledge on changes of properties with technological process including heat treatment and plastic working. The studied in this work copper CuTi4. CuFe2. CuCr0.7 and CuNi2Si1 alloys was selected to present differences in hardening phases .The samples were quenched, cold deformed (rolling), and aged. Detailed microstructure analysis and its influence on electrical and mechanical properties was presented in the work. Quenched CuTi4, CuFe2, CuCr0.7 and CuNi2Si1alloys have different mechanism and kinetics of precipitation during aging. These processes are complex and depend on the heterogeneity of distribution of alloying elements in copper matrix, the process parameters and cold strain value.

Keywords: hardened copper alloys, mechanical properties, electrical conductivity, microstructure

Wymagane cechy użytkowe których oczekuje się od stopów miedzi wywierają zasadniczy wpływ na ich technologiczny proces wytwarzania. Wynika stąd konieczność rozeznania zakresu zmian własności użytkowych wynikających z zastosowanego wariantu obróbki cieplnej i plastycznej. Stopy miedzi CuTi4, CuFe2, CuCr0.7 i CuNi2Si1 poddane badaniu w niniejszej pracy dobrano w ten sposób aby różniły się fazami umacniającymi. Próbki poddano przesycaniu, odkształceniu na zimno (walcowanie) oraz starzeniu. Przesycone stopy CuTi4, CuFe2, CuCr0.7 oraz CuNi2Si1 różnią się mechanizmem i kinetyką wydzielania podczas procesu starzenia. Procesy te są złożone i uzależnione od niejednorodności rozmieszczenia składników stopowych w osnowie miedzianej, historii wytwarzania i przetwarzania stopów, parametrów przesycania i starzenia jak tez wielkości odkształcenia na zimno.

1. Introduction

Popular copper alloys (e.g. bronzes and brasses) present much higher mechanical properties when compared to pure copper but their electrical and thermal conductivity is significantly lower. There is, however, a group of copper alloys able to be precipitation hardened in which, through proper selection of heat treatment and plastic working conditions, wide range of functional properties can be reached by formation of a required alloy microstructure. Deformation, especially cold one combined with processes of quenching and ageing is of fundamental importance since those operation can be used to influence formation of required microstructures and, in consequence, mechanical properties of the processed material.

The functional properties as required from the copper alloys have a fundamental influence on technology of their production, therefore there is a strong need to acquire knowledge on the range of functional properties changes resulting from application of a specific variant of heat treatment and plastic working. Another important factor lies in final dimensions of a product, especially its thickness and in dimension tolerances. Production scale, equipment, research methods significantly influence competitiveness, not only technical but also economical of the produced alloys [1-2].

There is a continuous quest for more perfect materials which, beside the required mechanical and physical properties, will be also reliable and durable in operation. Some compromise solutions can be reached with precipitation hardened copper alloys, often with application of combined heat and mechanical treatment. It is impossible, however, to reach in those alloys very high mechanical and electric or thermal properties at the same time. Depending on the relations between properties of those alloys the precipitation hardened copper alloys can be divided into two groups:

– copper alloys of high electrical (and heat) conductivity and elevated mechanical properties,

– copper alloys of moderate electrical (and heat) conductivity and high mechanical properties.

To reach optimal combination of electrical and heat conductivity and mechanical properties it is necessary to properly select components of the alloy with respect to their influence on mechanism and scale of hardening as well as on character of electrical conductivity changes. The developed principles for selection of alloying components for optimization of me-

* INSTITUTE OF NON-FERROUS METALS, UL. SOWIŃSKIEGO 5, 44-100 GLIWICE, POLAND
** INSITUTE OF ENGINEERING MATERIALS AND BIOMATERIALS, SILESIAN UNIVERSITY OF TECHNOLOGY, 18A KONARSKIEGO STR., 44-100 GLIWICE, POLAND

chanical and electrical properties in copper alloys [3-4] follow three criteria:

- Influence of alloying addition in solid solution on specific resistance of copper. The effect related to scattering of conductive electrons by precipitates in precipitation hardened alloys is practically negligible. The effect can be important with extremely small precipitates only, i.e. at the level of the size corresponding to cluster of atoms or GP zones. Also influence of vacancies, because of their low concentration in equilibrium conditions, can be omitted in practice. Conductivity of precipitation hardened alloys is therefore determined by concentration of alloying components in solid solution mainly, through Nordheim equation and taking under consideration Gibbs-Thomson relation which expresses equilibrium conditions as a function of the size of precipitates.
- Temperature dependency of solubility of alloying components in copper.
- Type, volumetric content and dispersion degree of the precipitated phases, which determine mechanism of alloy hardening (slitting or bypassing of precipitates by dislocations) and, in consequence, mechanical properties of a precipitation hardened alloy. Cold plastic deformation has a limited influence on electrical conductivity of copper and its alloys. Changes in conductivity resulting from the straining usually are lower than several MS/m.

Introduction of other atoms to the matrix of base metal results in hardening increase. The yield point of solid solution is higher than in pure metal [5]. That method of hardening, however, has some limitations. Much higher possibilities are created by hardening of the alloys with precipitated particles of new phases and that method is becoming more and more widely used. There is also a need for the precipitated particles to have a defined shape and size and to be uniformly distributed at appropriate distance between each other. Precipitation in structure defects, especially at grain boundaries, does not facilitate a complete exploitation of possibilities created by precipitation hardening.

Both local defects and precipitations of other phases have hampering effect on dislocation movement, in this way increasing the yield point. It was found out that energy of the admixture atom reaction with dislocation depends on its distance from the dislocation. This interaction leads to changes in concentration of these atoms in the neighborhood of the dislocation line. The increase of concentration of atoms surrounding a dislocation is called Cottrell atmosphere. The dislocation in the surface of the most dense packing of atoms in a regular face-centered lattice (A1) is instable and dissociates into two partial dislocations, bonded by the stacking fault. The latter can be considered a hexagonal phase plate in A1 lattice, and the boundary between those phases is a coherent boundary. Suzuki [6] took under consideration the state of thermodynamic equilibrium between a hexagonal layer of stacking fault and the other crystal, and proved that in the result of differences of energy the atoms of the admixtures should segregate in the ”stacking fault”. According to Suzuki foreign atoms are partly responsible for metal hardening effect, and that effect should be more visible at higher temperatures.

Presence of particles of second phase in the matrix leads to the yield point increase. The yield point increase depends on differences in the strength of a particle and matrix, structure of particle and matrix, dimensions, shape and character of precipitates, distribution of precipitated particles and distance between them.

The increaase of yield point is also significantly influenced by degree of coherence of precipitates with matrix and crystallographic interdependencies. To acquire knowledge on reasons of hardening of the alloy with precipitated particles it is necessary to take under consideration interactions between dislocations and particles.

Thermodynamic instability of multicomponent phase in a form of solid solution is the basic condition for precipitation to take place. The instability results in a tendency for its decomposition into new phases of different chemical composition. The precipitation reactions usually can be divided into three categories [7]:

– continuous precipitation
– localized precipitation
– discontinuous, cellular precipitation

According to that division a general pattern of the ways by which supersaturated solution turns into equilibrium phase mixture can be defined. The first way starts with localized precipitation on grain boundaries. Next the precipitation can be replaced by a slower process of continuous precipitation, which facilitates generation of a coherent transient phase. If in the result of continuous precipitation a stable phase is formed breaking of the coherence and gradual spheroidization takes place followed by coagulation of this phase. Growth of coherent transit phase brings stress increase in the matrix and its deformation. Sometimes it can may to discontinuous precipitation resulting from straining. The transit phase disappears to be replaced by equilibrium phase. In the final stage spheroidization and coagulation of the generated in the result of discontinuous precipitation particles of stable phase take place. The second way covers transformation in the temperature range in which volumetric diffusion of the dissolved atoms is slow enough for continuous precipitation not to take place. In that case decomposition of the solution occurs by discontinuous (cellular) precipitation and the diffusion distributes the admixture along the transformation front. A lamellar product of the transformation remains stable as long as the temperature is not high enough for spheroidization and coagulation to take place.

There are some practical instructions resulting from the above described patterns which can be used in improving the existing and developing new precipitation hardened copper alloys:

- High mechanical properties can be reached in alloys of large volumetric content of coherent precipitates, which are characterized by high energy of elastic strain at the matrix-precipitation interface (high degree of matrix and precipitate crystal lattice misfit and high shear modulus). In the case of incoherent precipitates, at constant content of hardening phase, the best mechanical properties are resulting from uniformly distributed systems of small precipitates.
- To reach good electrical conductivity in precipitation hardened alloys it is recommended for the precipitates to be in a form of pure alloying additions of high solubility in copper in quenching temperature and minimum solubility

in ageing temperature. The hardening effect in such alloys, e.g. Cu-Cr, Cu-Fe, Cu-Co (because of low solubility of Cr, Fe and Co in copper), however, is limited. According to the studies [8], that effect can be increased by application of rapid quenching of the alloy from the liquid state. The rapid quenching from the liquid state results in general structure refinement and, what is most important, provides possibility for metastable broadening of solubility limit of the alloying addition in solid solution and, therefore, for increase of the effect of precipitation hardening in ageing process. Formation of intermetallic compounds with copper by alloying additions is also advantageous.

- Application of alloying additions which form intermetallic phases with each other requires strict observation of stoichiometry, since any excess of the components reduces electrical conductivity of the alloy. The exception can be seen in intentional introduction of some of the components to produce additional hardening effect by reduction of stacking fault energy.
- Significant changes of mechanical properties while maintaining good electrical conductivity can be reached in processes of combined thermal and mechanical treatment. There is a need to pay attention, however, because the applied process parameter should not facilitate mechanism of discontinuous precipitation.

In the recent years the following alloys [9,10] from the group of precipitation hardened alloys have been manufactured on the wider scale:

Cu-Be which contains 0.5÷2 % Be,

Cu-Be-Ni and Cu-Be-Co which contain 0.2÷0.7 % Be and 1.5-5-2.8% Ni or Co. It should be noted that because of high toxicity of beryllium vapors that production disappears.

Cu-Ni-Si which contains 1÷3% Ni and 0.2÷1% Si often with tin addition in the range 0.1÷3% and/or magnesium addition in the range 0.05÷0.15.

Cu-Cr which contains 0.3÷1.2% Cr.

Cu-Cr-Zr which contains 0.3÷1.2% Cr and 0.02÷0.3% Zr,

Cu-Fe (most often 2% Fe) with small phosphorus addition.

Research studies addressed also multicomponent alloys of copper with Cr, Ni, Ti, Sn and Zr addition [11].

For those purposes also dispersion hardened materials are becoming more widely used, such as materials in copper matrix, special alloys in iron, nickel or chromium [12-13] or even precious metals [14-15] matrix.

This paper presents result of studies conducted with commercial copper alloys, such as CuTi, CuFe, CuCr and CuNiSi, able to be precipitation hardened. Influence of cold deformation after quenching on electrical conductivity of CuTi4, CuFe2, CuCr0.7 and CuNi2Si1 alloys and on kinetics of precipitation in those alloys was determined.

The alloys for studies were selected specifically to take under consideration the expected and diversified character of precipitation. While in the CuFe and CuCr alloys equilibrium or nonequilibrium precipitates of iron or chromium (A1 and A2 structure) can be present, in CuNiSi and CuTi alloys processes of supersaturated solution decomposition occur with formation of intermetallic phases. Additionally, in the first stages of the decomposition spinodal transformation takes place in CuTi alloy and ordering processes can be observed [16]. The studies were focused on changes in precipitation kinetics, especially in the relations between quenching and ageing, and quenching, cold deformation (applied to reduce zones free from precipitates in the areas of grain boundaries) and ageing, combined with investigations into changes of microstructure and functional properties.

An additional reason for selection of those alloys was their already existing and potential industrial application, mainly for current conducting elements operating at variable mechanical, current and heat loads. Strips from CuFe2 alloy are used in production of tracks in electronics, and strips of CuNi2Si1 and CuTi4 are mainly applied in production of resilient components for electronics and electrotechnics (switches, contacts, connectors). Chromium copper alloys (modified with various additions) are widely used as resistance welding electrodes, electrode holders, tips of welding torches, etc, while chromium copper strips are used in production, among others, of automotive radiators.

2. Methodology, material for studies

The initial material for the studies was in a form of samples of CuTi4, CuFe2, CuCr0.7 and CuNi2Si1 alloys cut out from a hot rolled strip of thickness about 4 mm. The samples were subjected to heat treatment and plastic working by:

a) – supersaturation by holding of CuTi4 alloy in temperature of 900°C, CuFe2 alloy in temperature of 950°C, CuCr0.7 alloy in temperature of 1000°C and CuNi2Si1 alloy in temperature of 950°C for 60 minutes and then rapid quenching in water,

b) – cold deformation (rolling) with 50% reduction and

c) – ageing of all alloys in temperature of 450°C, 500°C, 550°C and 600°C for 1, 2, 5, 10, 15, 30, 60, 120 and 420 minutes.

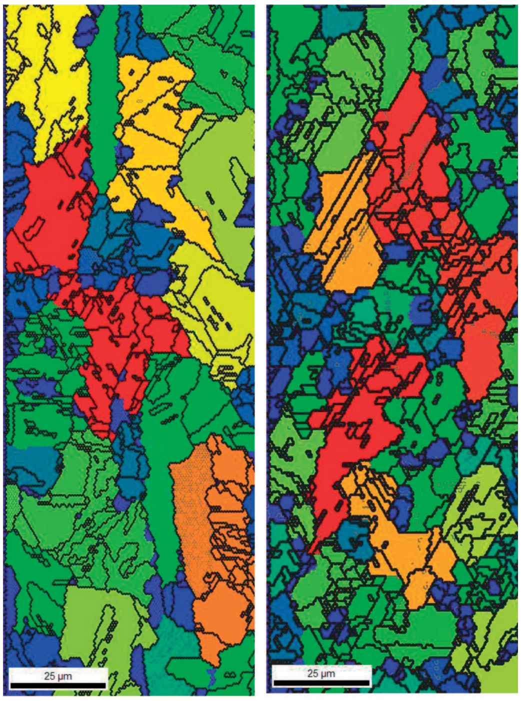
With thus selected conditions of heat treatment and plastic working material characteristics were developed. Results of studies into changes of electrical conductivity after ageing were used in analysis of mechanism and kinetics of precipitation in those alloys. Studies covered by variant c) were also used in determination of relations between precipitation and recrystallization processes in those alloys. Examination of microstructure was performed by electron transmission microscopy and EBSD method. Determination of electrical conductivity was done with Foerster Sigmatest.

3. Results and discussion

3.1. Microstructure after quenching, cold deformation with 50% reduction and ageing

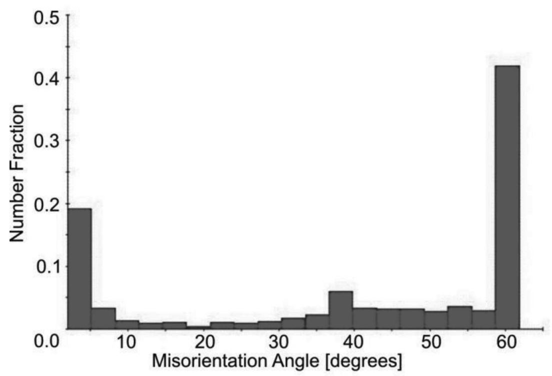
CuTi4 alloy

Ageing in temp. 550°C and 600°C of quenched and cold deformed CuTi4 alloy shows strong progress of recrystallization process, however already in the temperature of 450°C after 60 minute ageing 75% content of high angle grain boundaries was observed (Fig.1-2).

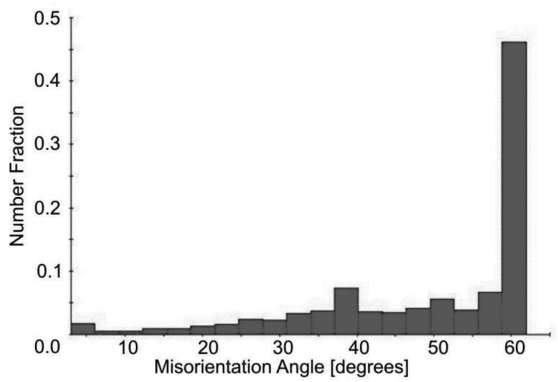


450°C/60 min. 600°C/60 min

Fig. 1. Maps of grain size in CuTi4 alloy - quenched, cold deformed with 50% reduction and aged in temperature of 450°C for 60 and in temperature 600°C for 60 minutes



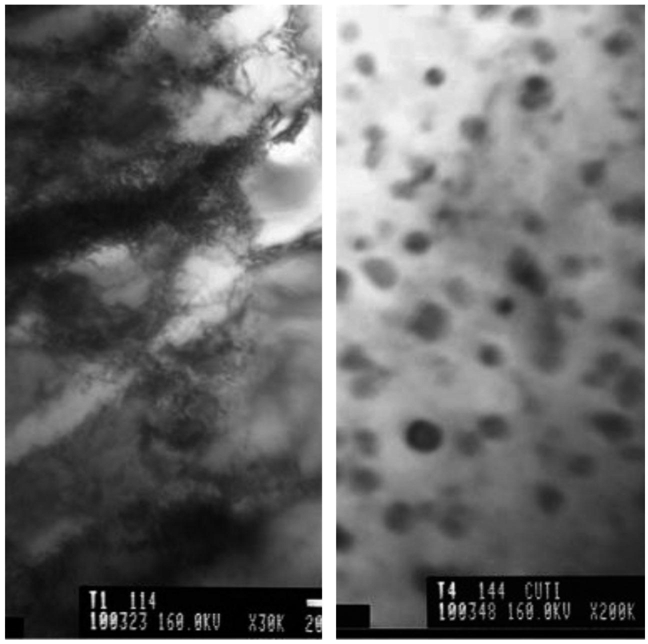
450°C/60 min.



600°C/60 min

Fig. 2. Distribution of misorientation angles of grain boundaries in CuTi4 alloy which was quenched, cold deformed with 50% reduction and aged in temperature 450°C and in temperature 600°C for 60 minutes

In microstructure of the alloy which was aged in temp. of 450°C for 1 minute continuous precipitation was observed. In longer ageing times discontinuous precipitation was observed at grain boundaries. Increase of ageing temperature to 500°C, 550°C and 600°C as well as ageing time brought domination of discontinuous precipitation. For example, after ageing in temp. 500°C for 60 minutes a modulated microstructure was observed, which is characteristic for spinodal transformation, and lamellar one, generated by nucleation of plates and their growth (Fig. 3).



450°C/60 min 600°C/60min

Fig. 3. Microstructure of CuTi4 alloy which ws quenched, cold deformed with 50% reduction and aged in temperature of 450°C and in temperature 600°C for 60 minutes

Increase of ageing time to 420 minutes resulted in dissolution of precipitated particles of the second phase. In quenched and aged, and in quenched, cold deformed (50% reduction) and aged alloy presence of Ti particles of micrometric size, not numerous Cu_3Ti particles and numerous Cu_4Ti particles of nanometric size was observed. It was found out that in the alloy which was quenched, cold deformed (50% reduction) and aged in temperature of 450°C recrystallization process was slower when compared to precipitation process. Cold deformation after quenching brings reduction of spinodal transformation temperature. The phase transitions which take place in the commercial CuTi4 alloy can be presented in the following way:

homogenous solid solution spinodal transformation chemical composition modulation <111>continuous ordering in the areas enriched with Ti metastable Cu_4Ti phase, ordered and coherent with matrix discontinuous transformation cellular microstructure, plates of Cu_3Ti or Cu_4Ti solid solution.

Such a phase transition pattern makes it impossible to describe precipitation kinetics in a simple way by Johnson-Mehl relation in the examined range of temperature and ageing time.

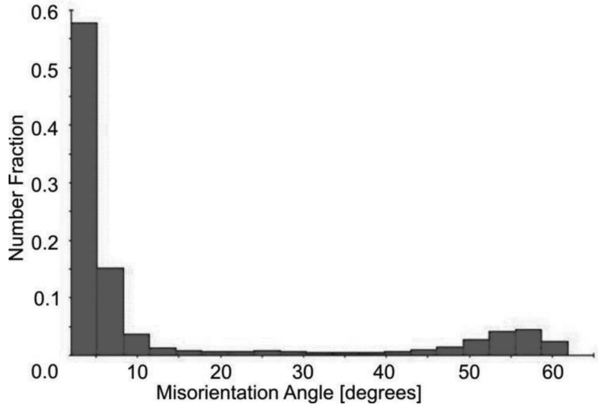
CuFe2 alloy

Application of cold deformation after quenching and ageing in the examined temperature (450°C, 500°C, 550°C and 600°C) in CuFe2 alloy (Fig. 4-5) helps to reach 63,21% extent of reaction in a short time (from 5-10 minutes, respectively). The cold deformation after quenching and ageing of CuFe2 alloy in temp. of 450°C for 60 minutes brings microstructure recovery only. In such conditions precipitation precedes recrystallization process (Fig. 3). It is only ageing in temp. 600°C for 60 minutes which leads to the complete recrystallization of the alloy.

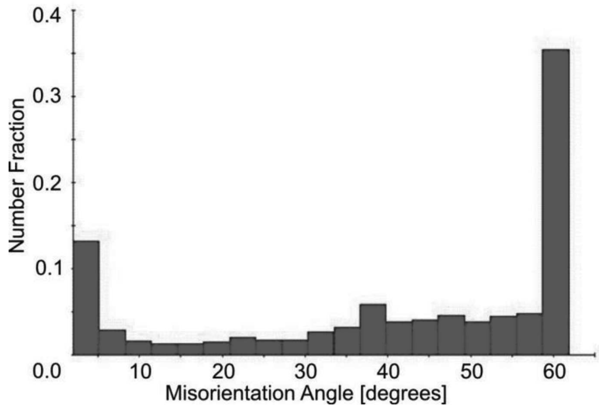
450°C/60 min 600°C/60 min

Fig. 4. Maps of grain size in CuFe2 alloy – quenched, cold deformed with 50% reduction and aged in temperature of 450°C for 60 and in temperature 600°C for 60 minutes

In the initial stages of ageing at the examined temperature (450°C, 500°C, 550°C and 600°C) in the period from 1 to 10 minutes, respectively, spherical and coherent with matrix iron particles of nonequilibrium A1 structure precipitate from supersaturated solution. The spherical shape of precipitates confirms control of morphology by surface energy of matrix-precipitate interface. The average diameter of particles for temp. of 550°C and ageing time of 10 min was 20 nm. After ageing for 120 minutes the diameter of precipitates increased to 50 nm, together with tendency for coherence degradation, most probably in the result of martenzite transformation. In microstructure of CuFe2 alloy also large iron particles of diameter ~200 nm were observed, which might have resulted from growth of heterogeneously nucleated iron precipitates of A2 structure (Fig. 6).

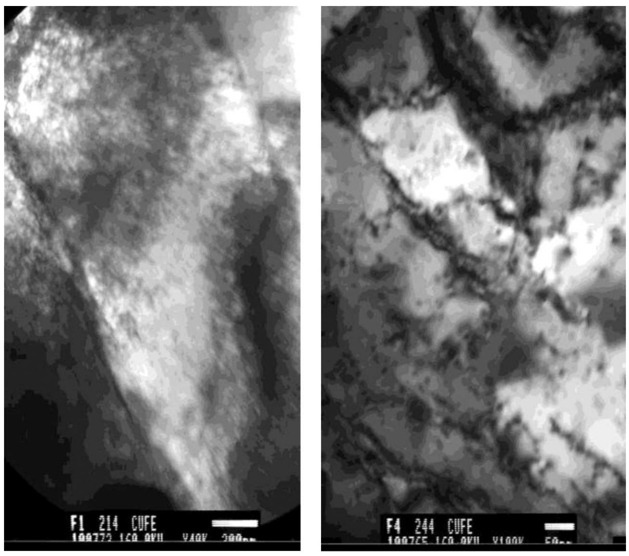


450°C/60 min.



600°C/60 min

Fig. 5. Distribution of misorientation angles of grain boundaries in CuFe2 alloy – quenched, cold deformed with 50% reduction and aged in temperature of 450°C and in temperature 600°C for 60 minutes



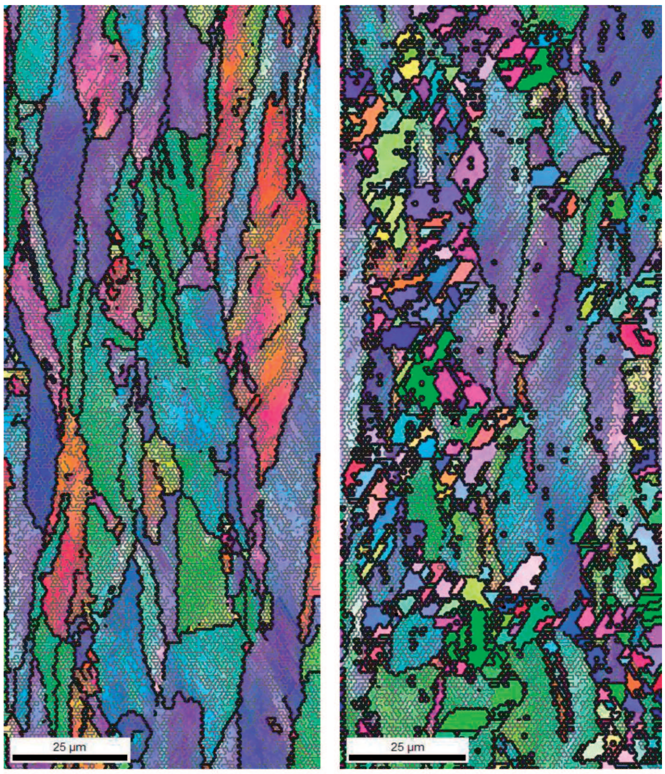
450°C/60 min 600°C/60 min

Fig. 6. Microstructure of CuFe2 alloy which was quenched, cold deformed with 50% reduction and aged in temperature of 450°C and in 600°C for 60 minutes

Quenching and ageing bring no significant hardening effect in CuFe2 alloy.

CuCr0.7 alloy

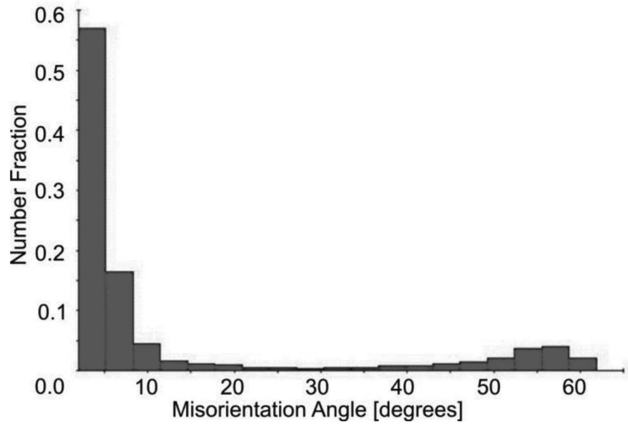
The changes in microstructure of CuCr0.7 alloy are similar to the ones in CuFe2 alloy. In the alloy which was aged in temp. of 450°C for 60 minutes no effects of recrystallization were observed, while ageing for 60 minutes in temperature of 600°C brings partial recrystallization of the alloy (Fig.7-8). Also in this case precipitation precedes recrystallization process.



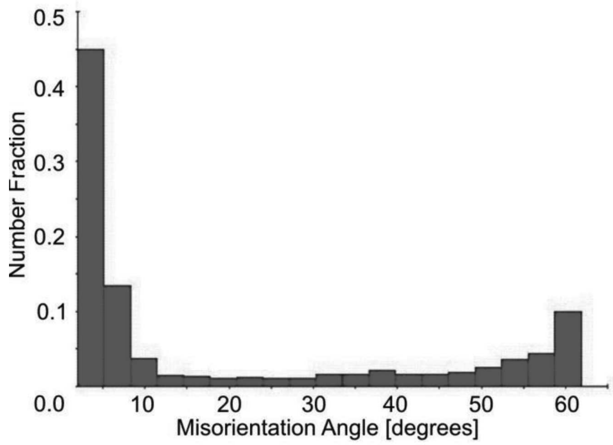
450°C/60 min. 600°C/60 min

Fig. 7. Maps of grain size in CuCr0.7 alloy – quenched, cold deformed with 50% reduction and aged in temperature of 450°C for 60 and in temperature 600°C for 60 minutes

During ageing of quenched alloy of copper and chromium spherical chromium particles precipitate, of nonequilibrium A1 structure and coherent with matrix (Fig. 9). The precipitation process is characterized by significant heterogeneity. In microstructure of the aged alloy some original, not dissolved during melting, chromium particles of diameter ~400nm, areas free from precipitates next to grain boundaries, twin boundaries, original precipitates as well as nucleation of precipitates in twin boundaries were observed. The ideal diameter of spherical precipitates is at the level of 6 – 8 nm. Bigger precipitates change their shape into ellipsoidal one while maintaining coherence of the precipitate with the matrix. For example, after ageing in temperature of 550°C for 10 minutes the average diameter of particles was 4,23 nm, after 30 min ageing the average diameter increased to 6,61 nm, after 120 minutes of ageing to 6,67 nm and after 420 minutes of ageing the average diameter was 10,13 nm. The microstructure produced in those conditions of heat treatment and plastic working is stable.

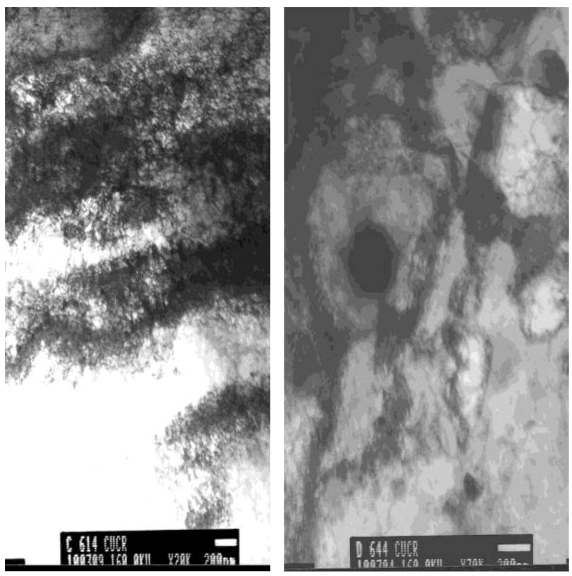


450°C/60 min.



600°C/60 min

Fig. 8. Distribution of misorientation angles of grain boundaries in CuCr0,7 alloy which was quenched, cold deformed with 50% reduction and aged in temperature of 450°C and in temperature 600°C for 60 minutes



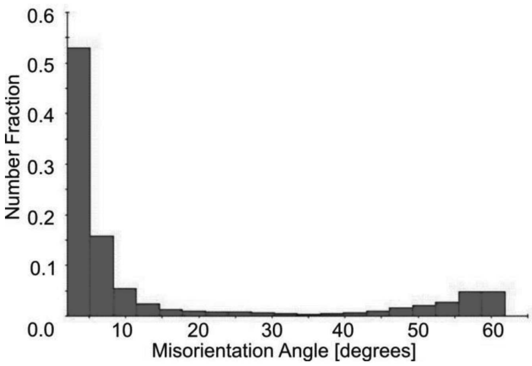
450°C/60 min 600°C/60 min

Fig. 9. Microstructure of CuCuCr0,7 alloy which was quenched, cold deformed with 50% reduction and aged in temperature of 450°C and in 600°C for 60 minutes

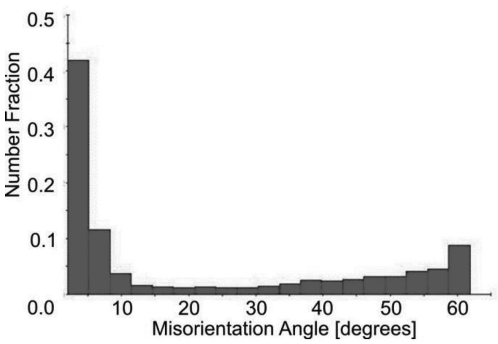
CuNi2Si1 alloy

450°C/60 min. 600°C/60 min

Fig. 10. Maps of grain size in CuNi2Si1 alloy- quenched, cold deformed with 50% reduction and aged in temperature of 450°C for 60 and in temperature 600°C for 60 minutes



450°C/60 min.

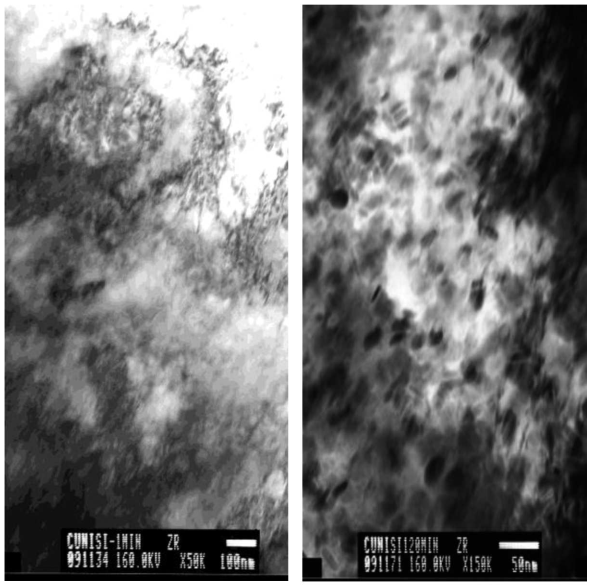


600°C/60 min

Fig. 11. Distribution of misorientation angles of grain boundaries in CuNi2Si1 alloy which was quenched, cold deformed with 50% reduction and aged in temperature of 450°C and in temperature 600°C for 60 minutes

During ageing of CuNi2Si1 in temperature of 450°C for 60 minutes beginning of recrystallization is observed, while after ageing in temperature of 600°C for 60 minutes completely recrystallized microstructure is registered, however of significantly heterogeneous grain size (Fig.10-11). Overlapping of precipitation and recrystallization processes in that alloy can therefore be supposed.

Decomposition of quenched alloy takes place directly by precipitation of the equilibrium Ni_2Si phase. Form of "disc" is a privileged shape of precipitates which proves that the process is controlled by energy of elastic strain of interface. After ageing in temperature of 550°C for 120 minutes the average diameter of Ni_2Si precipitates is in the range 20-30 nm, while the thickness is of several nm (Fig. 8). Prolongation of the ageing results in transformation of "disc" precipitates into thin tetra- or polygonal plates. Depending on ageing temperature and time a certain size range of precipitated Ni_2Si particles (which differ by several orders of magnitude) was observed in copper matrix, with the largest content of the smallest, nanometric particles (Fig. 12).



450°C/60 min 600°C/60 min

Fig. 12. Microstructure of CuNi2Si1alloy which was quenched, cold deformed with 50% reduction and aged in temperature of 450°C and in temperature 600°C for 60 minutes

3.2. Electrical conductivity after quenching, cold deformation with 50% reduction and ageing of CuTi4, CuFe2, CuCr0.7, CuNi2Si1 alloys

Table 1 shows electrical conductivity of the examined alloys.

Table 1 presents only two variants of heat treatment since the lowest hardness in all examined alloys was reached after ageing in temperature of 450°C for 1 min, and the highest after ageing in temperature of 550°C for 420 minutes. High conductivity in CuFe2 (34.2 MS/m) and CuNi2Si (15.7 MS/m) alloys was reached in ageing at 500°C for 420 min.

Such broad ranges of changes in electrical conductivity can be linked to the microstructure of alloys which was formed after heat treatment and plastic working and resulting from different hardening mechanisms and different kinetics of phase precipitation from quenched, quenched and cold deformed copper alloys in ageing process.

TABLE 1
Results of examination of electrical conductivity of copper alloys after application of various variants of heat treatment and plastic working

Electrical conductivity MS/m				
alloy	quenching	quenching and 50% deformation	quenching, 50% deformation and ageing	
			450°C/1 min.	550°C/420 min
CuTi4	2.8	2.5	3.4	11
CuFe2	15.4	9.5	10.3	34.8
CuCr0.7	20.5	18	18.3	49.4
CuNi2Si1	8.5	7.7	8.6	15.7

In general it can be stated that hardness peaks are observed in early stages of ageing, while increase of electrical conductivity is connected to longer ageing times. Such course of changes of hardness and electrical conductivity is confirmed by the presented results of microstructure examination. High density of very fine, nanometric precipitates, uniformly distributed in copper matrix results in strong hardening of the alloy. Such microstructure does not create favorable conditions for reaching high electrical conductivity. Therefore, depending on the planned application, the developed data can be used in selection of advantageous parameters of heat treatment and plastic working of those alloys to reach a determined state and stability of microstructure.

4. Dependencies used to describe precipitation kinetics

Kinetics of phase transitions in heterogeneous systems can be unusually complex and it is difficult to describe it by simple dependencies. It was established empirically that in many cases the extent of reaction can be described by the following relation:

$$y = 1 \exp\left[-(K \cdot t)\right]^n \tag{1}$$

where:

y – extent of reaction, $0 \leqslant y \leqslant 1$
K – reaction rate constant
t – time
n – exponent

The dependency is known as Johnson-Mehl equation or as Avrami relation. To verify whether the precipitation process complies with Johnson-Mehl equation the equation has to be modified into the linear form. The dependency has linear character in a relevant coordinate system in which n and K are constant throughout the transformation, however there are situations when n and K change in the process.

If n and K are constant and assuming:

$$K = \frac{1}{\tau} \tag{2}$$

where:

τ – time constant
the equation can be presented in another form

$$y = 1 - \exp - \left(\frac{t}{\tau}\right)^n \tag{3}$$

Exponent n and time constant τ can be determined by using double logarithmic function. In that way we can produce:

$$\log\log\left(\frac{1}{1-y}\right) = n\log t - n\log\tau - \log 2.303 \tag{4}$$

By plotting the results in the coordinate system of $\log\log\frac{1}{1-y}$ and $\log\tau$ axes a straight line is produced of slope n and staring ordinate:

$$b = n\log\tau - \log 2.303 \tag{5}$$

From which we can calculate:

$$\log\tau = -\frac{b + \log 2.303}{n} \tag{6}$$

The relation between time constant and temperature is expressed by:

$$\tau = C \cdot \exp\frac{Q_\tau}{R \cdot T} \tag{7}$$

When the relation is presented in coordinate system of $\log\tau$ and inverse of a temperature expressed in kelvin a straight line is produced, and from its slope activation energy Q_τ of precipitation process can be calculated.

The presented method that the exponent and time constant can be calculated from direct or indirect measurements of extent of reaction for isothermal conditions. The activation energy of precipitation process can be also calculated from other dependencies, such as rate of growth of precipitates.

To verify whether precipitation kinetics in the examined alloys can be described by those relations the results of studies into changes of electrical conductivity generated by quenching and ageing processes were used.

In the studies strong influence of cold deformation after quenching on kinetics of processes taking place during ageing was established. Figures 13-16 present comparison of TTT diagrams for extent of reaction y = 0.6321 in individual alloys.

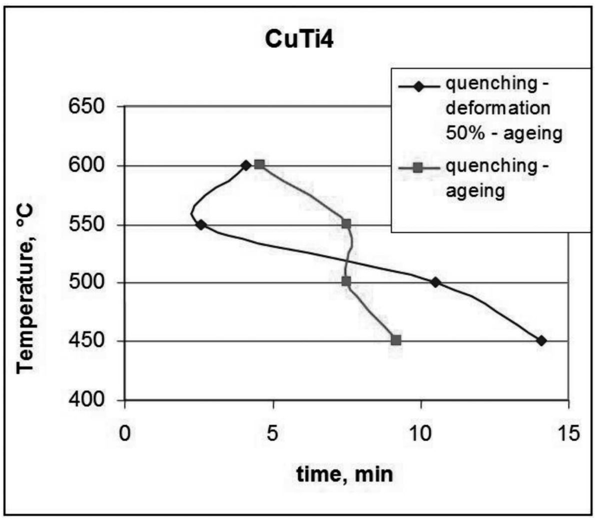


Fig. 13. TTT diagram for CuTi4 alloy after quenching and ageing, and after quenching, cold deformation (50% reduction) and ageing; extent of reaction y = 0.6321

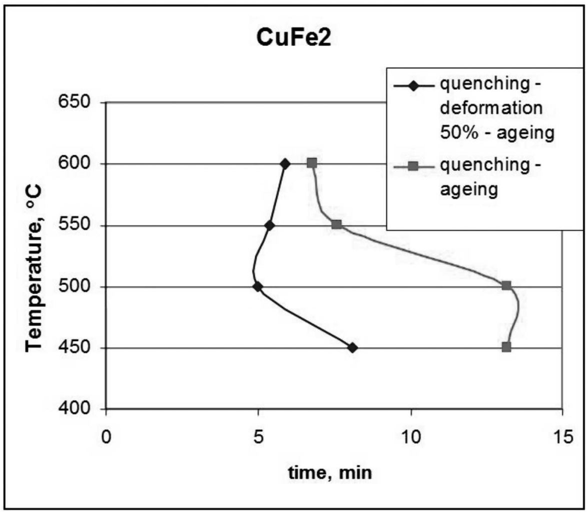


Fig. 14. TTT diagram for CuFe2 alloy after quenching and ageing, and after quenching, cold deformation (50% reduction) and ageing; extent of reaction y = 0.6321

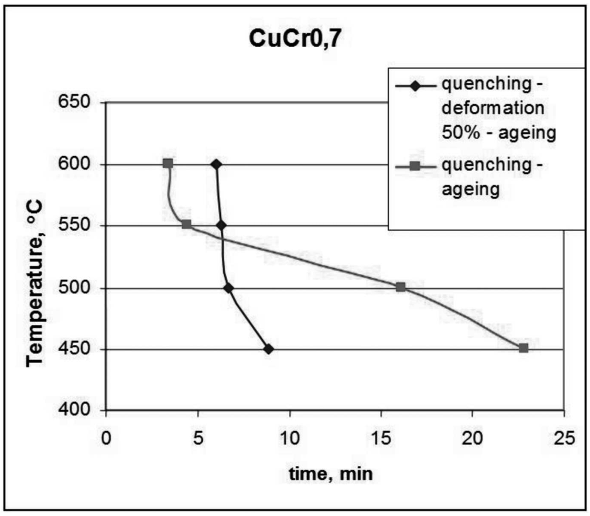


Fig. 15. TTT diagram for CuCr0.7 alloy after quenching and ageing, and after quenching, cold deformation (50% reduction) and ageing; extent of reaction y = 0.6321

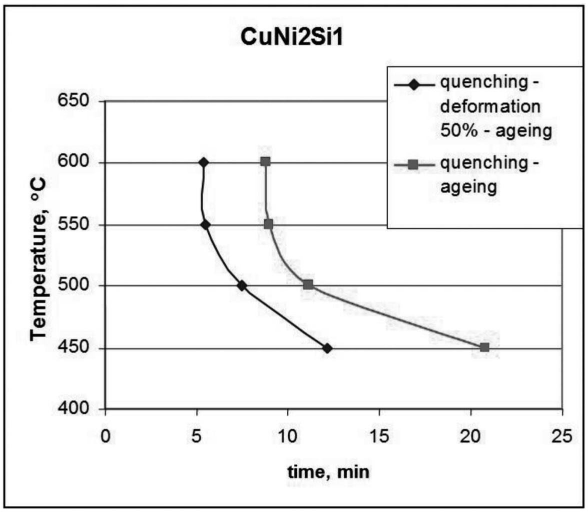


Fig. 16. TTT diagram for CuNi2Si1 alloy after quenching and ageing, and after quenching, cold deformation (50% reduction) and ageing; extent of reaction y = 0.6321

5. Conclusions

Copper alloys CuTi4, CuFe2, CuCr0.7 and CuNi2Si1 were selected specifically to present differences in the hardening phases. In the CuTi4 alloy, depending on conditions of quenching and ageing, spinodal decomposition can take place by precipitation of transient phases to equilibrium Cu_4Ti phase, or by discontinuous precipitation of that phase. Iron and chromium precipitate in copper and CuFe2 and CuCr0.7 alloys during ageing process in a nonequilibrium (of A1 structure) or equilibrium (of A2 structure) form. During ageing of CuNi2Si1 alloy intermetallic Ni_2Si phase precipitate.

The role of the applied cold deformation (50% reduction) after quenching of the examined alloys is illustrated by the presented maps of distribution of misorientation and grain size produced by EBSD method. Cold deformation of quenched CuFe2 and CuNi2Si1 alloys speeds up precipitation in the examined temperature range (450°C, 500°C, 550°C and 600°C). The precipitation process overlaps with progressing recrystallization. Ageing of CuTi4 alloy in temperature of 550^0C and 600^0C shows strong progress of recrystallization, however after 60 minutes of ageing in temperature of 450°C already 75% content of high angle grain boundaries was registered. Application of cold deformation after quenching and ageing in examined temperature (450°C, 500°C, 550°C and 600°C) in CuFe2 alloy helps to reach the extent of reaction of 63.21% in a short time (5-10 minutes, respectively). Influence of cold deformation after quenching and ageing of CuFe2 alloy in temperature of 450°C for 60 minutes results in microstructure recovery only. In such conditions precipitation precedes recrystallization process. It is only ageing in temp. of 600°C for 60 minutes which leads to the complete recrystallization of the alloy. The changes in microstructure of CuCr0.7 alloy are similar to the ones in CuFe2 alloy. In the alloy which was aged in temp. of 450°C for 60 minutes no effects of recrystallization were observed, while ageing in temp. of 600°C for 60 minutes brings partial recrystallization of the alloy. Also in this case precipitation precedes recrystallization process. During ageing of CuNi2Si1 in temperature of 450°C for 60 minutes beginning of recrystallization is observed, while after ageing in temperature of 600°C for 60 minutes completely recrystallized microstructure is registered, however of significantly heterogeneous grain size. It can be suspected that there is overlapping of precipitation and recrystallization processes in that alloy.

Broad ranges of changes in mechanical properties (hardness mainly) and electrical conductivity can be linked to the microstructure of alloys which was formed after heat treatment and plastic working and resulting from different hardening mechanisms and different kinetics of phase precipitation from quenched, quenched and cold deformed copper alloys in ageing process.

High density of very fine, nanometric precipitates, uniformly distributed in copper matrix results in strong hardening of the alloy. Such microstructure does not create favorable conditions for reaching high electrical conductivity. Therefore, depending on the planned application, the developed data can be used in selection of advantageous parameters of heat treatment and plastic working of those alloys to reach a determined state and stability of microstructure.

Strong influence of cold deformation after quenching on kinetics of processes taking place during ageing was established in the studies.

The developed results of the investigations into changes of mechanical properties, electrical conductivity and microstructure of the alloys together with processes of charge preparation, melting and casting, hot plastic working, quenching, ageing, and quenching-cold deformation-ageing sequence represent a strong basis which provide possibilities to reach required functional properties by formation of their stable microstructure.

- Advantageous combinations of mechanical properties and electrical conductivity can be reached in the commercial copper alloys able to be precipitation hardened by proper selection of volumes of alloy components, both with respect to their influence on mechanism and scale of hardening and on character of electrical conductivity changes, especially on difficulties related to maintaining optimal level of impurities.

- Quenched CuTi4, CuFe2, CuCr0.7 and CuNi2Si1 alloys present different mechanism and kinetics of precipitation during ageing, especially after quenching, cold deformation and ageing. These processes are complex and depend on the heterogeneity of distribution of alloying elements in copper matrix, history of alloy production and processing, parameters of quenching and ageing, as well as cold strain value both after quenching and before ageing, and after quenching and ageing. The study demonstrated changes of exponent n and constant K of Johnson-Mehl equation for those alloys which proves that kinetics of precipitation from supersaturated solid solutions in those alloys is complex and heterogeneous.

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