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Thermomechanical processing of CuTi4 alloy

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Materials

ABSTRACT

Purpose: One of the reasons behind the interest in copper titanium alloys was development of new materials to substitute copper beryllium alloys. The reason for selecting that material for studies was that in the early stages of decomposition of CuTi4 alloy a spinodal transformation takes place and ordering processes begin. Proper selection of heat treatment and plastic working conditions provides possibilities to produce very wide range of sets of properties by formation of the required alloy microstructure. Therefore the main objective of the study was to capture the changes in precipitation kinetics, especially in the relations between supersaturation and ageing or between supersaturaion, cold deformation and ageing in connection to the changes in microstructure and functional properties (mainly changes in hardness and electrical conductivity).
Design/methodology/approach: Melting of the charge material was conducted in medium-frequency induction furnace, in a graphite crucible. The melted material after bath preparation was poured into a cast iron ingot mould (with graphite grease applied on the inside) of dimensions 35 x 120 x 250 mm. The ingots after casting were peeled. The treated ingots were heated in resistance furnace at 900ºC for 1.5 hour and rolled down on a reversible two-high mill.
Findings: Decomposition of supersaturated solid solution in that alloy is similar to the alloys produced in laboratory scale. The observed differences in microstructure after supersaturation were related to the presence of undissolved Ti particles and increased segregation of titanium distribution in copper matrix including microareas of individual grains. The mentioned factors influence the mechanism and kinetics of precipitation and subsequently the produced wide ranges of functional properties of the alloy.
Research limitations/implications: Cold deformation (50% reduction) of the alloy after supersaturation changes the mechanism and kinetics of precipitation and provides possibilities for production of broader sets of functional properties. It is expected that widening of the cold deformation range should result in more complete characteristics of material properties, suitable for the foreseen applications. Similar effects can be expected after application of cold deformation after ageing.
Practical implications: The elaborated research results present some utilitarian qualities since they can be used in development of process conditions for industrial scale production of strips from CuTi4 alloy of defined properties and operating qualities.
Originality/value: The mentioned factors influence the mechanism and kinetics of precipitation and subsequently the produced wide ranges of functional properties of the Cu-Ti alloys.
Keywords: Metallic alloys; Mechanical properties; Electrical properties

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1. Introduction

Precipitation hardening is partly associated with the studies of A. Wilm conducted since 1901 to increase mechanical properties of aluminium alloys [1]. The first results of the studies were presented in 1911 in a form of quality assessment. Analytical techniques of that time did not provide possibilities to explain the hardening processes in a satisfactory way. However in 1919 it was widely acknowledged that the main reason for the hardening of supersaturated alloys is precipitation process which develops with time, called ageing. It was only in 1938 that Guinier and Preston independently determined presence of characteristic dispersion of X-rays during examination of aged aluminium alloys, resulting from formation of clusters of Cu atoms in supersaturated solid solution. Existence of the clusters - Guinier-Preston (G-P) zones - was confirmed in 1953, by transmission electron microscopy methods.

Tensile strength increase of copper in the process of precipitation hardening is higher than in the solution hardening. Additional precipitation of second phase particles from supersaturated solid solution results in lower concentration of the alloying element of the well conductive matrix which facilitates electrical conductivity increase of the alloy. Therefore a compromise between mechanical properties and electrical conductivity can be reached in the alloys which show variable with temperature solubility of alloying components in the solid state.

Precipitation hardening is a heat treatment process composed of supersaturation and ageing. The necessary condition for the supersaturation to take place is heating the alloy at the temperature exceeding *solvus* line for a certain period of time. The objective is to maintain homogenous solid solution. Then, by rapid cooling down to room temperature a metastable supersaturated solid solution is produced. Decomposition of the supersaturated solution takes place during ageing process at a room or elevated temperature. Complete insolubility of alloying components in copper alloys at a low temperature (up to 500°C) and strong temperature dependency of their solubility in high temperature improves tensile strength and electrical conductivity. Production of large sets of properties depends mainly on:

- type and concentration of alloying additions,
- temperature dependency of solubility of alloying additions,
- morphology of precipitates,
- dispersion and relative volume of precipitated particles.

High tensile strength depends on the type of generated precipitates, which in extreme cases can be coherent or incoherent with the matrix. There are two mechanisms for dislocations to get through the second phase precipitates, presenting obstacles which hamper their movement. The particles are either cut across by the dislocations or bypassed. Both these mechanisms function in coherent and incoherent particles. Lack of coherence between a particle and matrix makes difficult or even impossible for the dislocations to cut across. The degree of interactions between particles and moving dislocation depends on size of particles and distance between them.

The basic condition for precipitation process to take place is thermodynamic instability of supersaturated solid solution. The instability results in tendencies to decomposition of the solution and precipitation of particles of new phase with different chemical composition and crystal structure. The most often observed precipitates in those reactions are [2]:

- continuous,
- localized,
- discrete, cellular.

Such a division provides possibilities for presentation of a general pattern of supersaturated solid solution transition into equilibrium phase mixture. There are two transition patterns. The first starts with precipitation of second phase particles on the grain boundaries. Next, this precipitation becomes substituted with a slow process of continuous precipitation which facilitates formation of a coherent transition phase. In the result of the continuous precipitation particles of stable phase are generated, and then breaking of their coherence with matrix, gradual spheroidization and coagulation of particles take place. Growth of coherent particles of transition phase results in increase of stresses in the matrix and its deformation which can lead to discrete precipitation. The transition phase disappears to be replaced by the equilibrium phase. The final stage of that transition pattern is coalescence of stable phase particles generated during discrete precipitation.

The second pattern of transition takes place at the temperature range in which volumetric diffusion of dissolved atoms is low and there is no continuous precipitation. Decomposition of the solution takes place by discrete (cellular) precipitation. In the result of diffusion process atoms of alloying elements move along the transition front. Lamellar precipitates generated during the transformation change their morphology with temperature increase in the processes of spheroidization and coagulation.

The described precipitation processes which favour production of good hardness and electrical conductivity are presented for CuTi4 alloy.

The maximum solubility of titanium in copper is 8 at% at a temperature of 885°C (Fig. 1).

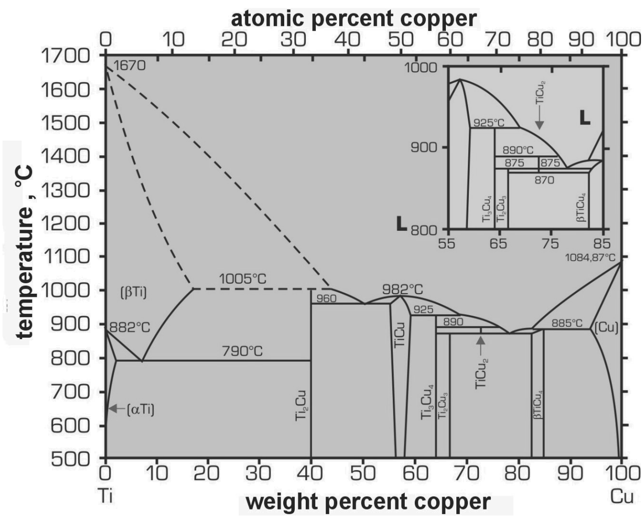


Fig. 1. Phase equilibrium system Ti-Cu [3]

Metastable intermediate phases of orderly structure can be generated in that range before precipitation of particles of equilibrium phase βTiCu4. Between the melting point of particles of TiCu phase and eutectic temperature of transition (73 at% Cu) peritectic reactions are observed which lead to formation of intermetallic phases of stoichiometric formulae Ti_3Cu_4 (57.1 at% Cu), Ti_2Cu_3 (60 at% Cu), $TiCu_2$ (66.7 at% Cu) and $TiCu_4$ (78-80.9 at% Cu). In copper-titanium alloys two equilibrium phases of $TiCu_4$ are present. Stable phase β and metastable phase α which, after long time of ageing even at a low temperature, undergoes transformation into phase β. There are some premises about possibilities of phase β transition during cooling down into a stable phase α at a low temperature. Alloys of high copper content are hardened during ageing (Fig. 2).

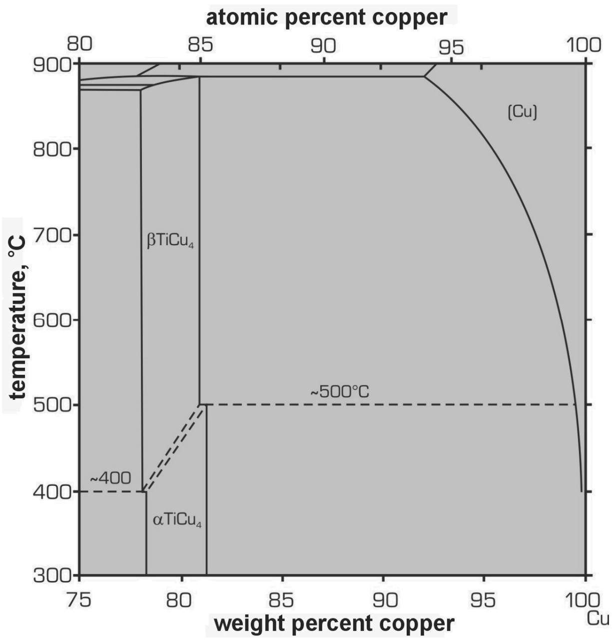


Fig. 2. Fragment of phase equilibrium system Ti-Cu [3]

2. Material for studies

One of the reasons behind the interest in copper titanium alloys was development of new materials to substitute beryllium copper. Production of beryllium copper is troublesome because of high toxicity of beryllium and difficulties in its production and processing. It was also established that there is a possibility to produce wide range of functional properties of copper titanium alloys after application of certain heat treatment and plastic working. Studies into mechanism and kinetics of precipitation were performed on commercial copper alloy CuTi4 which can be precipitation hardened [4]. The reason for selecting that material for studies was that in the early stages of decomposition of CuTi4 alloy a spinodal transformation takes place and ordering processes begin. Proper selection of heat treatment and plastic working conditions provides possibilities to produce very wide ranges of sets of properties by formation of the required alloy microstructure. Therefore the main objective of the study was to capture the changes in precipitation kinetics, especially in the relations between supersaturation and ageing and between supersaturaion, cold deformation and ageing in connection to the changes in microstructure and functional properties (mainly changes in hardness and electrical conductivity).

Melting of the charge material was conducted in medium-frequency induction furnace, in a graphite crucible. The melted material afetr bath preparation was poured into a cast iron ingot mould (with graphite grease applied on the inside) of dimensions 35 x 120 x 250 mm. The ingots after casting were peeled. The treated ingots were heated in resistance furnace at a temperature of 900°C for 1.5 hour and rolled down on a reversible two-high mill. Hardness of the cast CuTi4 alloy on its section transverse to casting direction was HV267 while its electrical conductivity γ = 9.02 MS/m. After hot rolling from thickness of 40 mm down to 3.0 mm, the values were HV288 and γ = 7.48 MS/m, respectively. The hot rolled alloy was supersaturated (soaking - temperature 900°C/1hour, quenching in water) and aged (ageing temperature: 450°, 500°, 550° and 600°C, duration: 1, 5, 10, 15, 30, 60, 120 and 420 minutes). The average hardness after supersaturation was HV125, while average electrical conductivity γ = 2.80 MS/m. Values of other mechanical properties were in the ranges as follows:

- R_m from 685 to 695 MPa;
- $R_{0.2}$ from 574 to 589 MPa;
- $R_{0.05}$ from 436 to 476 MPa;
- A from 9 to 9.5 %.

From the hot rolled strips a suitable number of samples was cut out to be used in further investigations.

3. Studies into micro-structure and functional properties of CuTi4 alloy

The microstructure of CuTi4 alloy after supersaturation is coarse-grained with high number of twin boundaries as well as undissolved small particles of Ti (Figs.3, 4).

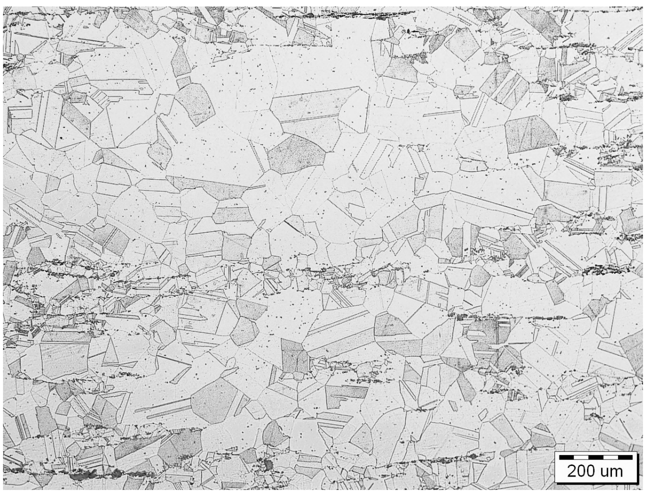


Fig. 3. Microstructure of CuTi4 alloy after supersaturation (900^0C/1h/water)

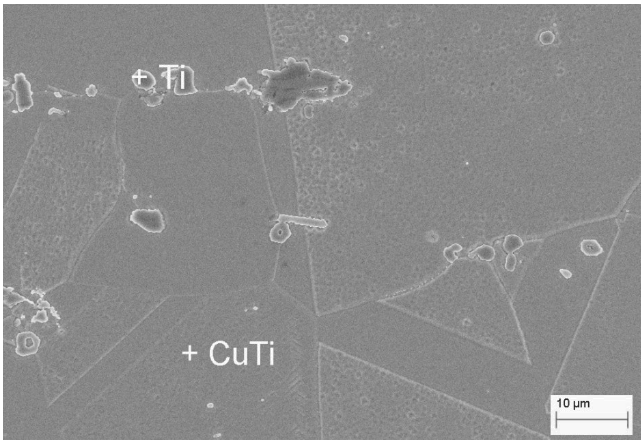


Fig. 4. Microstructure of CuTi4 alloy after supersaturation, + zones of chemical microanalysis (EDS)

Ageing of supersaturated commercial CuTi4 alloy (Fig. 5) at a temperature of 450^{0}C results in increase of its hardness with the increase of ageing time. The hardness increases from the level of HV125 (after supersaturation) to HV250 (ageing time 7 hours). When temperature of ageing is 500°C hardness of HV250 can be reached after 2 hours already. The increase of ageing time leads to hardness reduction. When increasing the ageing temperature to 550°C hardness of HV230 can be reached after 0.5 h, while in the ageing temperature of 600°C maximum hardness HV280 is reached after 10 minutes. At the same time the increase of ageing time leads to rapid reduction of alloy hardness to HV180.

Hardness HV and electrical conductivity γ of supersaturated CuTi4 alloy change with temperature and ageing time (Figs. 5 ,6).

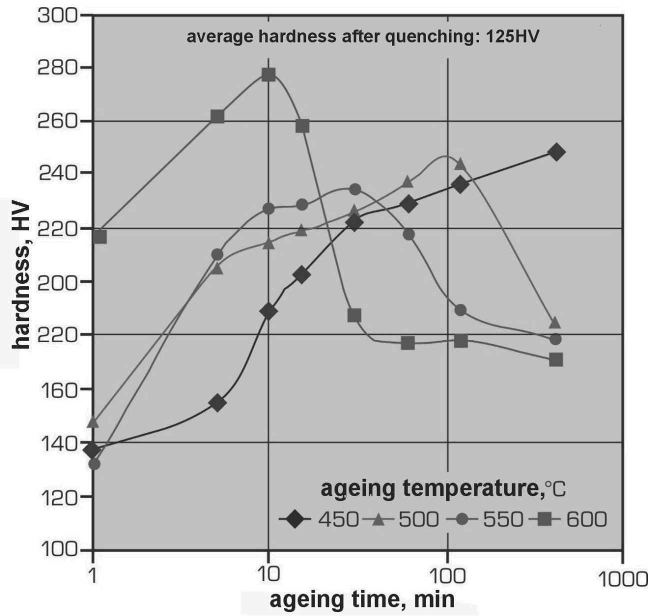


Fig. 5. Hardness of supersaturated CuTi4 alloy vs. temperature and ageing time

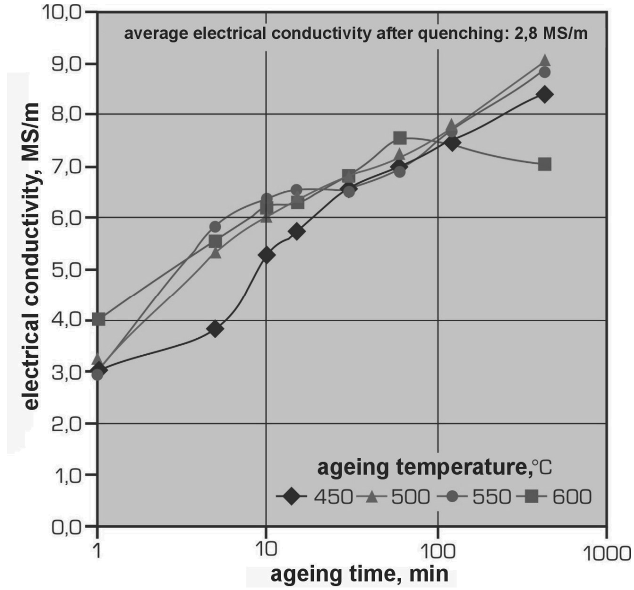


Fig. 6. Electrical conductivity γ of supersaturated CuTi4 alloy vs. temperature and ageing time

Supersaturation and ageing of commercial CuTi4 alloy in specific ranges of temperature and time result in increase of electrical conductivity from the level of 2.80 MS/m after supersaturation to about 9.0 MS/m after ageing at a temperature of 450°C for 7 hours. Ageing at a temperature of 600°C brings different changes in electrical conductivity, which increases for 2 hours of ageing. Prolonged ageing time results in its decrease.

Also microstructure of CuTi4 alloy changes during ageing process. For example, after ageing at a temperature of 500°C for 1 hour a modulated microstructure was observed, which is characteristic for spinodal transformation (Fig. 7), as well as a lamellar one, created by nucleation and growth of nuclei (Fig. 8).

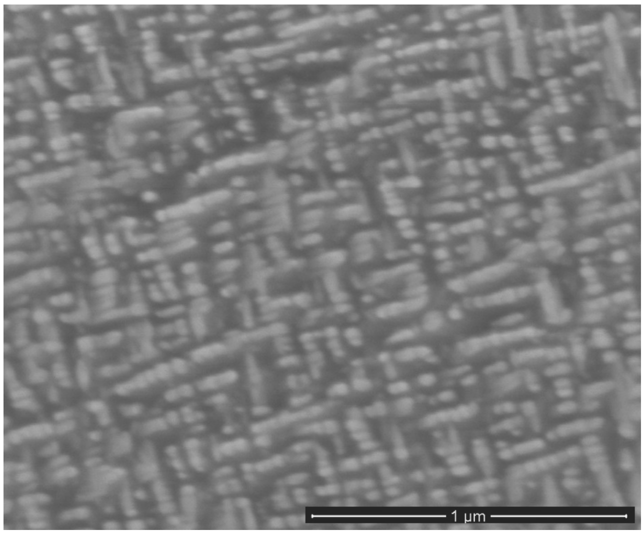


Fig. 7. Microstructure of CuTi4 alloy after supersaturation and ageing (500°C/1h)

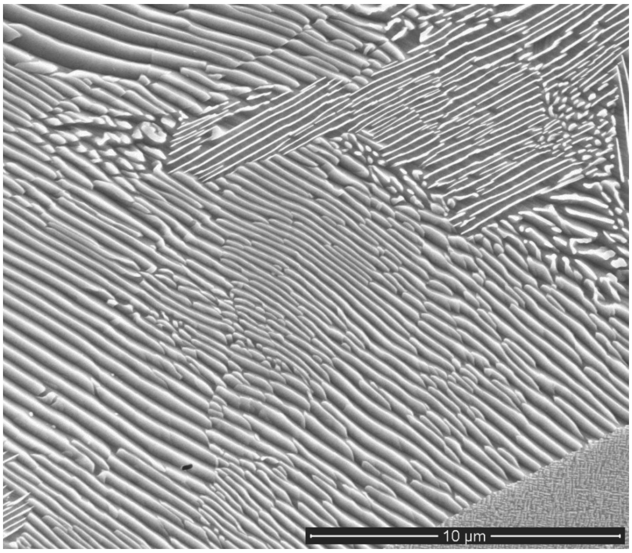


Fig. 8. Microstructure of CuTi4 alloy after supersaturation and ageing (500°C/1h). Conspicuous lamellar precipitates

In those ageing conditions both continuous and discrete precipitation processes were observed in CuTi4 alloy (Fig. 9).

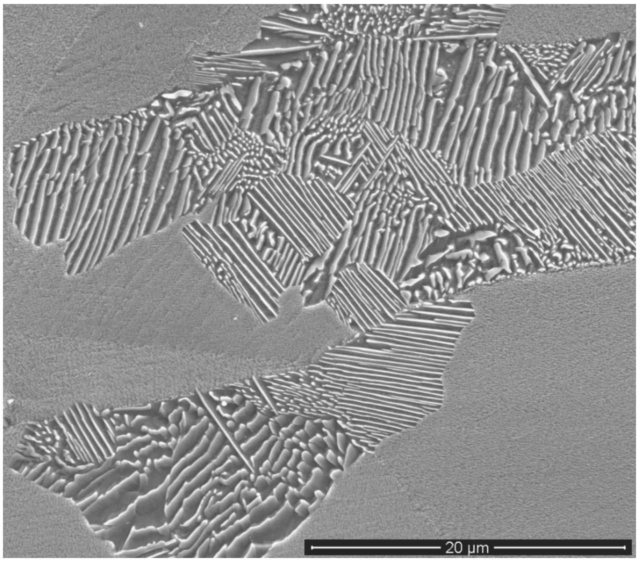


Fig. 9. Microstructure of CuTi4 alloy after supersaturation and ageing (500°C/1h) Conspicuous areas of continuous and discrete precipitation

After application of electron microscopy methods in the observation of microstructure of CiTi4 alloy which was aged at a temperature of 500°C large influence of ageing time on morphology and dimensions of precipitated particles of second phase was observed (Figs. 10-12).

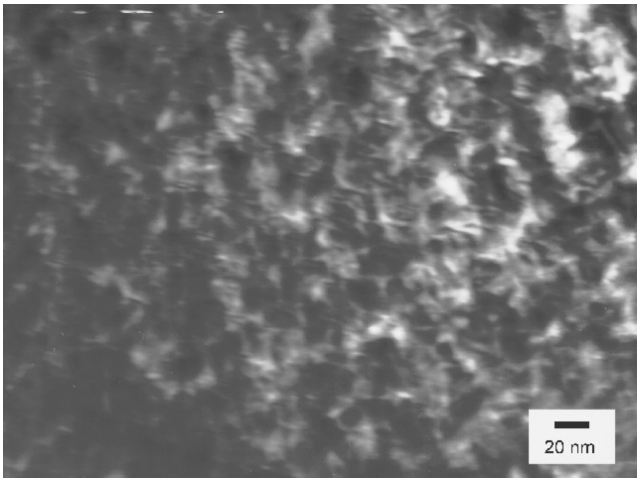


Fig. 10. Microstructure of CuTi4 alloy after supersaturation and ageing (500°C/10 min.). Conspicuous small precipitates of second phase

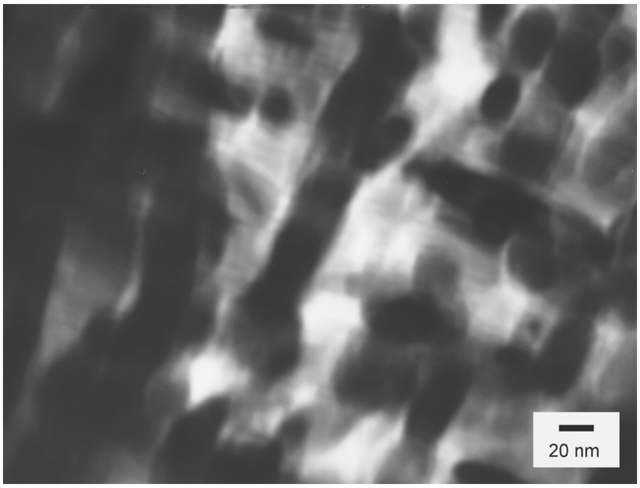


Fig. 11. Microstructure of CuTi4 alloy after supersaturation and ageing (500°C/0.5 h). Conspicuous growth of precipitates

The increase of CuTi4 alloy ageing time leads to dissolutin of precipitated particles of second phase (Fig. 12). At the same time hardness of the alloy decreases. Decomposition of supersaturated solid solution of CuTi4 alloy is complex and not homogenous. When ageing takes place at a temperature of 550°C the decomposition runs according to two mechanisms: continuous and discrete precipitation. The influence of both mechanisms depends on ageing time. After short ageing time (up to about 2 hours) evident zones of precipitates related to continuous precipitation are still observed (according to the mechanism: supersaturated solid solution – transition phases – equilibrium phase). After longer ageing times the whole microstructure area is covered by the products of discrete precipitation in a form of alternately layered lamellae of Cu_4Ti phase and the matrix. Figs. 13 and 14 show kinetics of extent of reaction in relation to temperature and ageing time of supersaturated CuTi4 alloy.

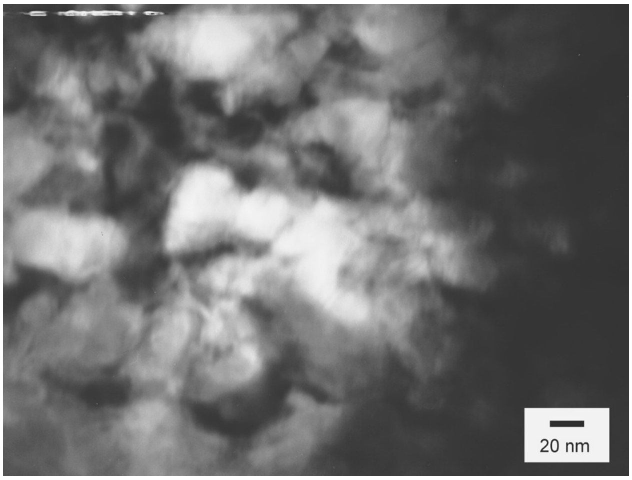


Fig. 12. Microstructure of CuTi4 alloy after supersaturation and ageing (550 C/7h) Conspicuous part of dissolved precipitates

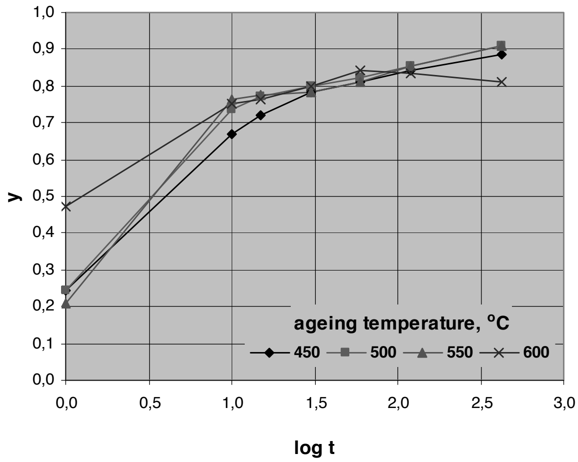


Fig. 13. Changes in extent of reaction *y* vs. temperature and ageing time of supersaturated CuTi4 alloy

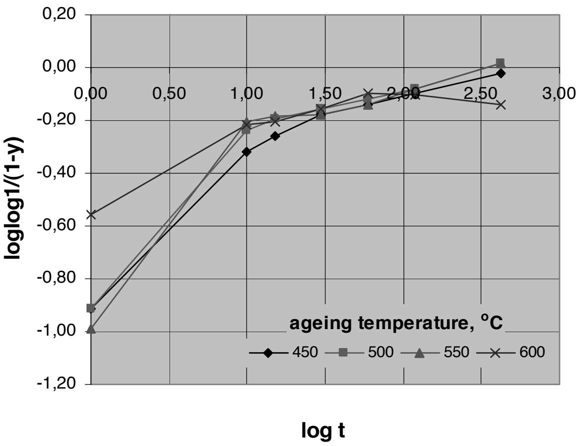


Fig. 14. Dependency between loglog 1/(1-y) and log t of supersaturated CuTi4 alloy in various ageing temperatures

Interesting results were produced with CuTi4 alloy when after supersaturation cold deformation (50% reduction) and ageing were applied. Figures 15 and 16 show kinetics of extent of reaction in relation to temperature and ageing time of supersaturated and cold deformed after supersaturation CuTi4 alloy.

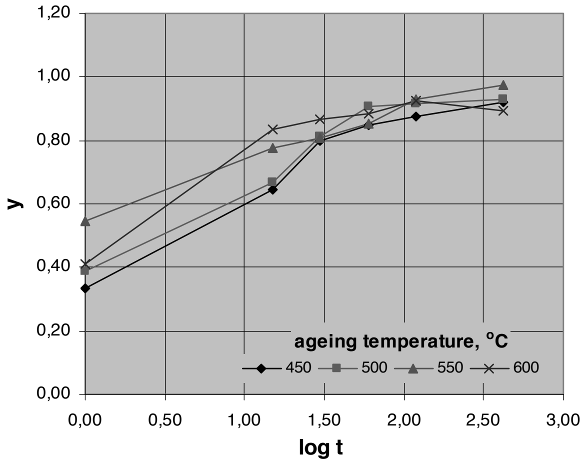


Fig. 15. Changes in extent of reaction *y* vs. temperature and ageing time of supersaturated and cold deformed (50% reduction) CuTi4 alloy

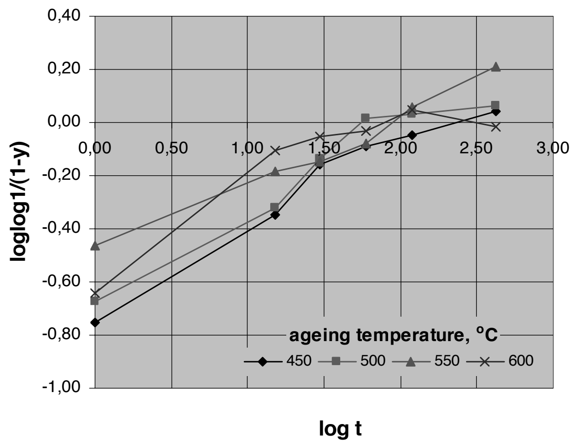


Fig. 16. Dependency between loglog 1/(1-y) and log t of supersaturated and cold deformed (50% reduction) CuTi4 alloy in various ageing temperatures

To show more clearly the differences in the observed phenomena a comparison of the changes in hardness, electrical conductivity and microstructure of the alloy in two variants of heat treatment and plastic working was made.

4. Comparison of the results from studies into hardness and electrical conductivity after supersaturation and ageing as well as after supersaturation, cold deformation (50% reduction) and ageing

To present more clearly the influence of cold deformation after supersaturation on hardness and electrical conductivity of CuTi4 alloy after ageing Figures 17-20 present their changes in relation to temperature and ageing time.

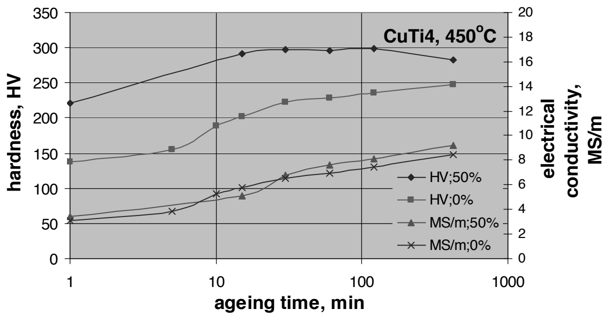


Fig. 17. Changes of hardness and electrical conductivity after supersaturation and ageing, and after supersaturation, cold deformation (50%) of ageing of CiTi4 alloy for ageing temperature of 450°C

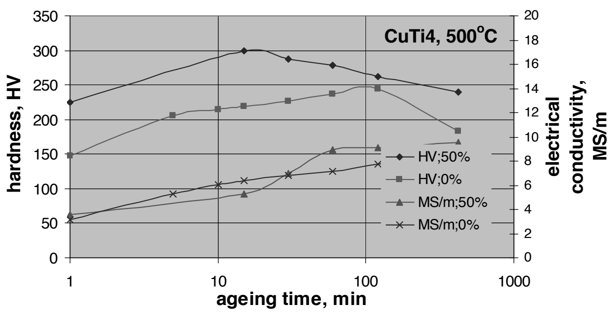


Fig. 18. Changes of hardness and electrical conductivity after supersaturation and ageing, and after supersaturation, cold deformation (50%) and ageing of CiTi4 alloy for ageing temperature of 500°C

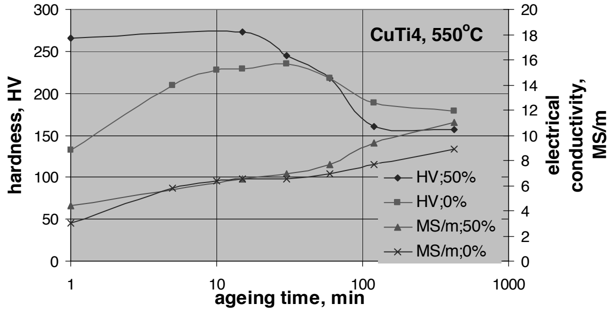


Fig. 19. Changes of hardness and electrical conductivity after supersaturation and ageing, and after supersaturation, cold deformation (50%) or ageing of CiTi4 alloy for ageing temperature of 550°C

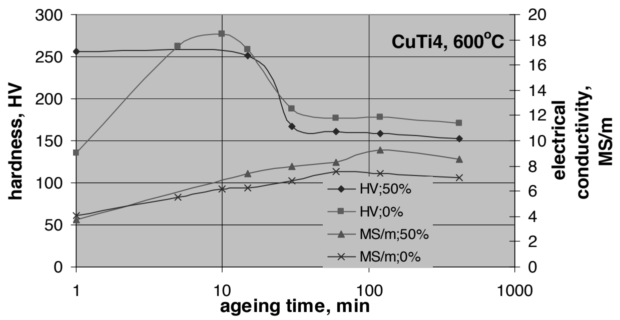
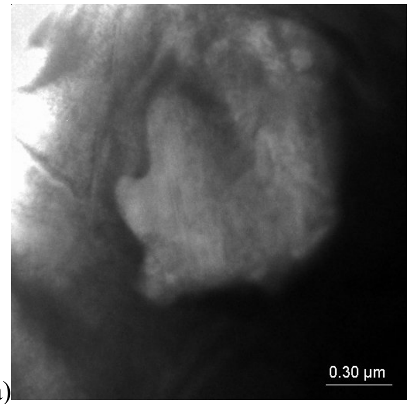
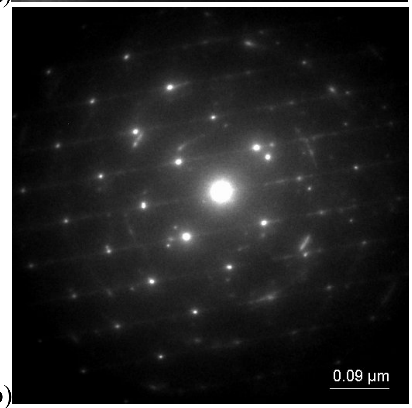


Fig. 20. Changes of hardness and electrical conductivity after supersaturation and ageing, and after supersaturation, cold deformation (50%) or ageing of CiTi4 alloy for ageing temperature of 600°C

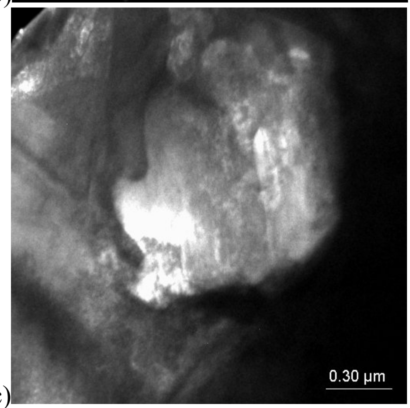
The presented in Figs. 17-20 dependencies show that application of cold deformation (50% reduction) after supersaturation can result in better sets of functional properties after ageing when compared to the alloy which was not cold deformed after supersaturation. The observed differences are shown in the images of alloy microstructure presented in Figs. 21-25.



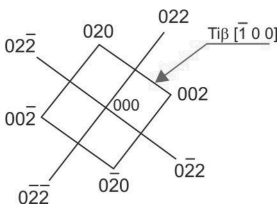
a)



b)



c)



d)

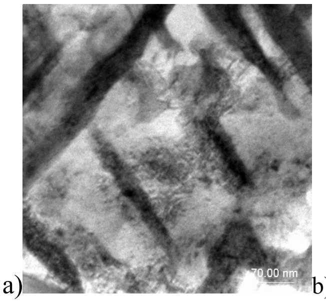
Fig. 21. Microstructure of supersaturated, cold deformed (50% reduction) and aged (550°C/1 min.) CuTi4 alloy. Original, undissolved Ti particle

a) – image in bright field;

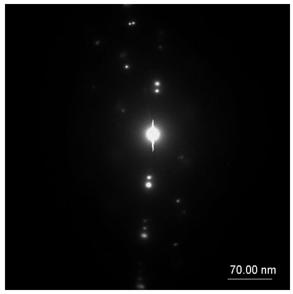
b) – diffraction pattern of the area from Fig. a);

c) – image in dark field from $00\bar{2}$ reflection of Ti (A2 lattice);

d) – solution of the diffraction pattern in Fig. b)



a)



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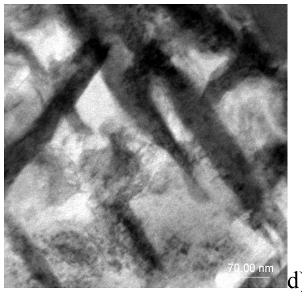
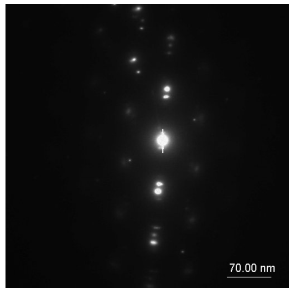
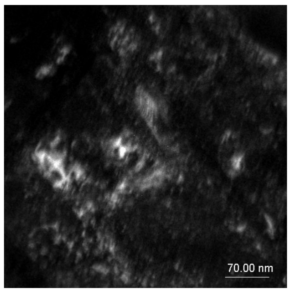


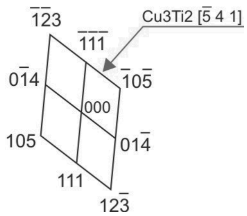
c)



d)



e)



f)

Fig. 22. Microstructure of supersaturated, cold deformed (50% reduction) and aged (550°C/1 min.) CuTi4 alloy. Cu_3Ti_2 precipitate

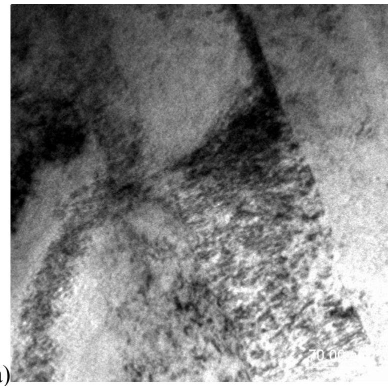
a) – c) image in bright field;

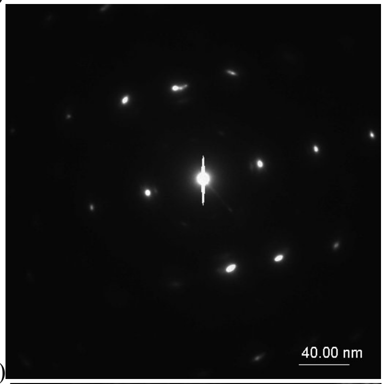
b) – diffraction pattern of the area from Fig a)

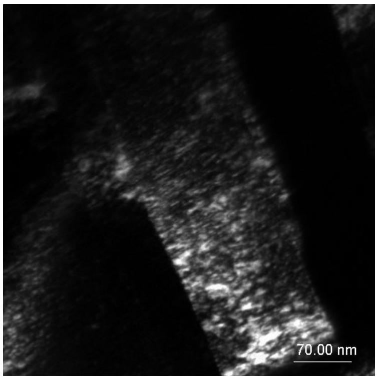
d) – diffraction pattern of the area from Fig c);

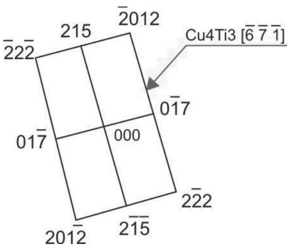
e) – image in dark field from 111 reflection of Cu_3Ti_2

f) – solution of the diffraction pattern in Fig. d

a) 

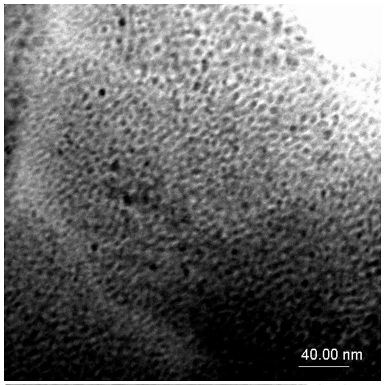
b) 

c) 



d)

Fig. 23. Microstructure of supersaturated, cold deformed (50% reduction) and aged (550°C/1 min.) CuTi4 alloy
a) – image in bright field;
b) – diffraction pattern of the area from Fig. a);
c) – image in dark field from $2\bar{1}\bar{5}$ reflection; Cu_4Ti_3, tetragonal lattice;
d) – solution of the diffraction pattern from Fig. b

a) 

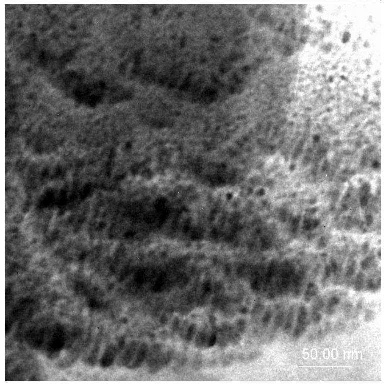
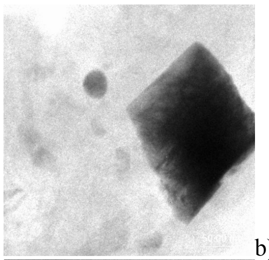
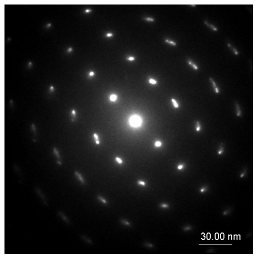
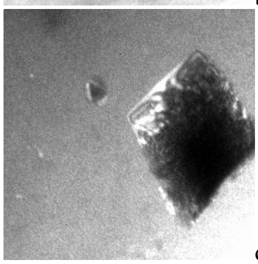
b) 

Fig. 24. Microstructure of supersaturated, cold deformed (50% reduction) and aged (550°C/1 min.) CuTi4 alloy; image in bright field; conspicuous areas of discrete precipitation a), and area of continuous precipitation b)

a) 

b) 

c) 

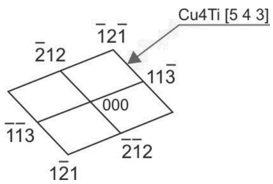
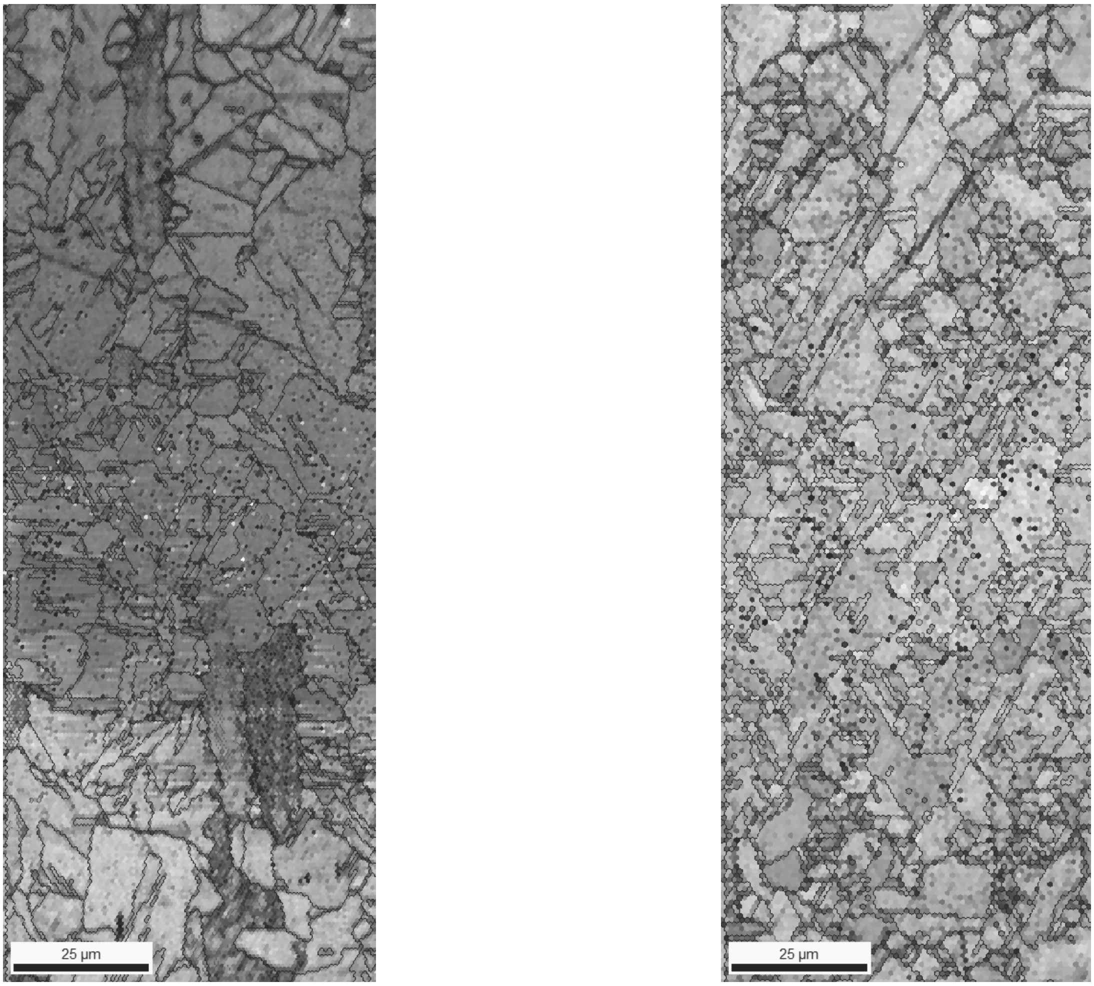
d) 

Fig. 25. Microstructure of supersaturated, cold deformed (50% reduction) and aged (550°C/1 min.) CuTi4 alloy
a) – image in bright field;
b) – diffraction pattern of the area from Fig. a);
c) – image in dark field from $\bar{2}12$ reflection of Cu_4Ti, orthorhombic lattice;
d) – solution of the diffraction pattern from Fig. b);

5. Influence of cold deformation after supersaturation on recrystallization of CuTi4 alloy

Application of cold deformation after supersaturation strongly influences on changes in hardness and electrical conductivity after ageing. Ageing of supersaturated and deformed by cold rolling (50% reduction) CuTi4 alloy at a temperature of 450°C results in gradual increase of hardness to the level of about HV300 after 30 minutes of ageing. The reached level of hardness holds for the ageing time of 420 minutes. It is a prove of properties stability in similar operating conditions. When holding that alloy at a temperature of 500°C the hardness of HV300 is reached after 15 minutes of ageing (hardness peak). Prolongation of the ageing time leads to monotonic decrease of hardness to the level of HV240 after 420 minutes of ageing. Ageing at a temperature of 550°C and 600°C does not provide possibilities to reach high hardness of CuTi4 alloy. Hardness of the alloy after its ageing for 420 minutes at a temperature 550°C reaches HV157, while at a temperature 600°C reaches HV152. It can be seen as a proof of overlapping of recrystallization processes with precipitation (Figs. 26-30).



450°C/60 min. 600°C/60 min.

Fig. 26. Grain boundary misorientation in CuTi4 alloy supersaturated, cold deformed with 50% reduction and aged at a temperature of 450°C for 60 minutes and at a temperature of 600°C for 60 minutes

Ageing 450°C/60 min

Angle range	content
___ from 2° to 5°	0.188
___ from 5° to 15°	0.060
___ from 15° to 180°	0.752

Ageing 600°C/60 min

Angle range	content
___ from 2° to 5°	0.048
___ from 5° to 15°	0.021
___ from 15° to 180°	0.931

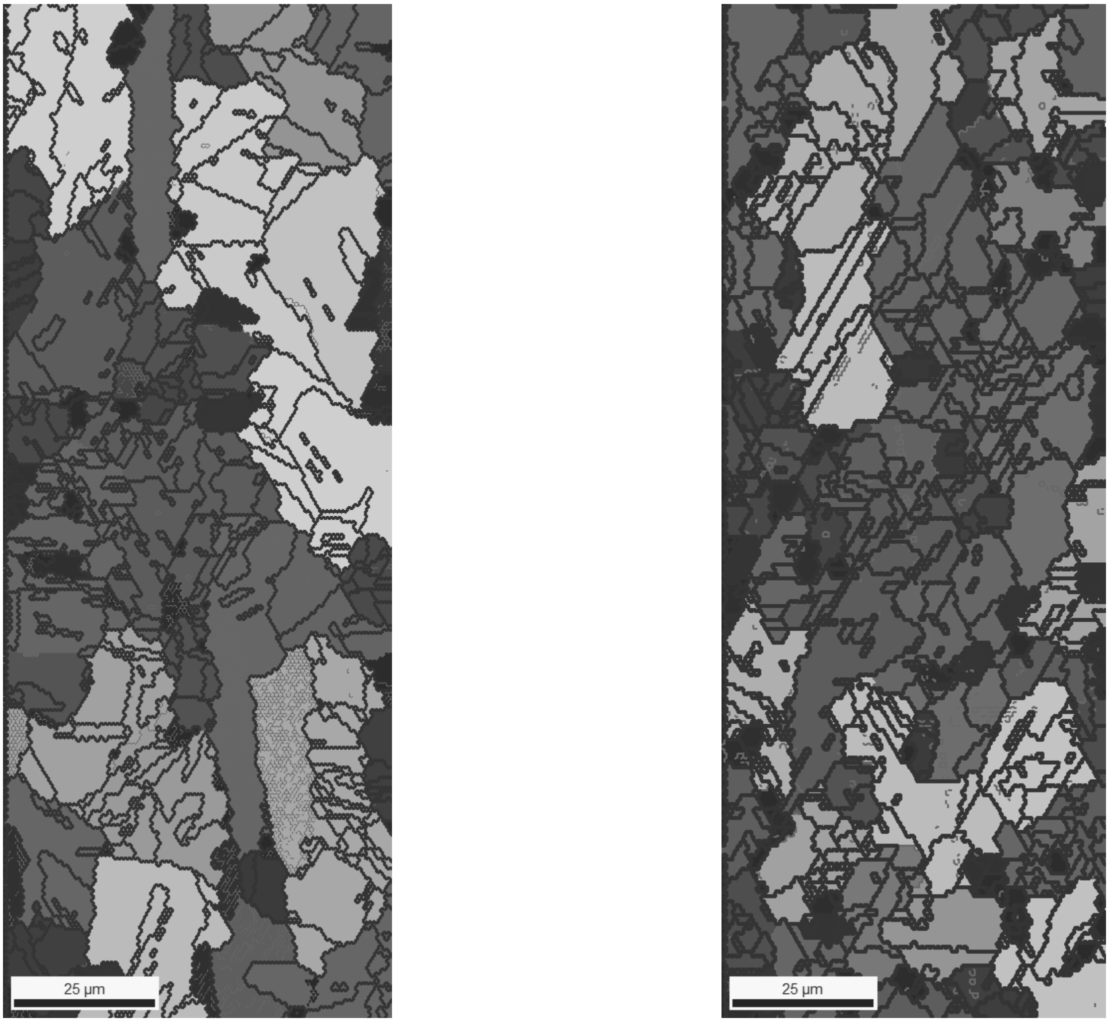


Fig. 27. Grain size distribution in CuTi4 alloy supersaturated, cold deformed with 50% reduction and aged at the temperature of 450°C for 60 minutes and at a temperature of 600°C for 60 minutes

Ageing 450°C/60 min

Angle range	content
from 2° to 15°	0.248
from 15° to 180°	0.752

Ageing 600°C/60 min

Angle range	content
from 2° to 15°	0.076
from 15° to 180°	0.924

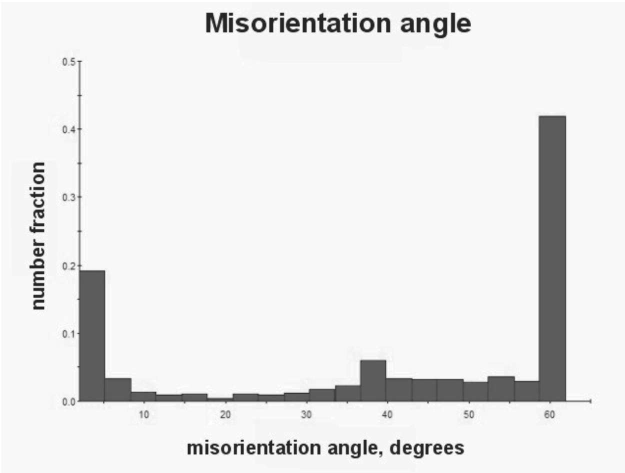


Fig. 28. Grain boundary misorientation angle distribution in CuTi4 alloy supersaturated, cold deformed with 50% reduction and aged at a temperature of 450°C for 60 minutes

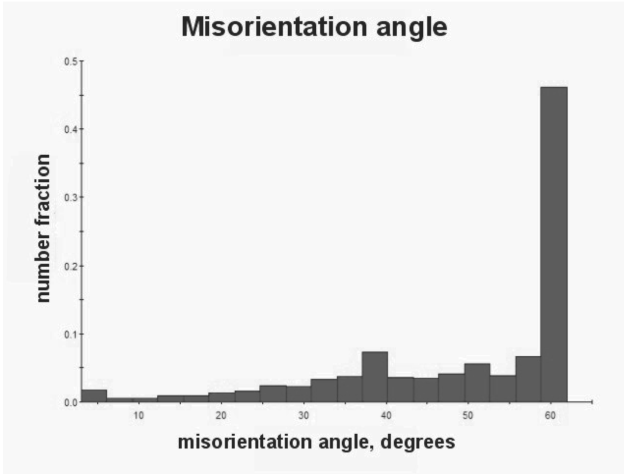
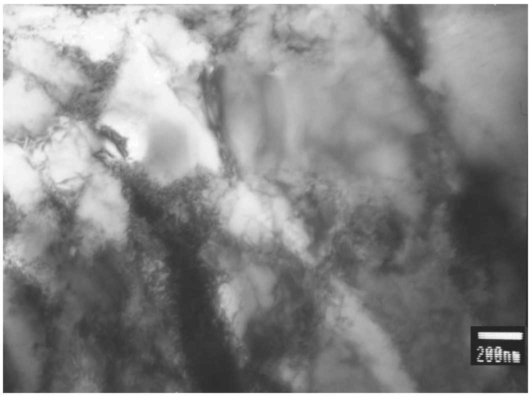
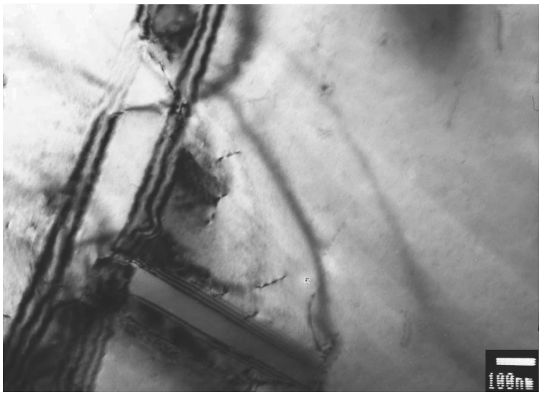


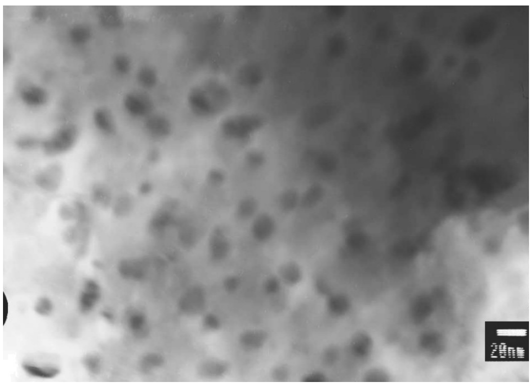
Fig. 29. Grain boundary misorientation angle distribution in CuTi4 alloy supersaturated, cold deformed with 50% reduction and aged at a temperature of 600°C for 60 minutes



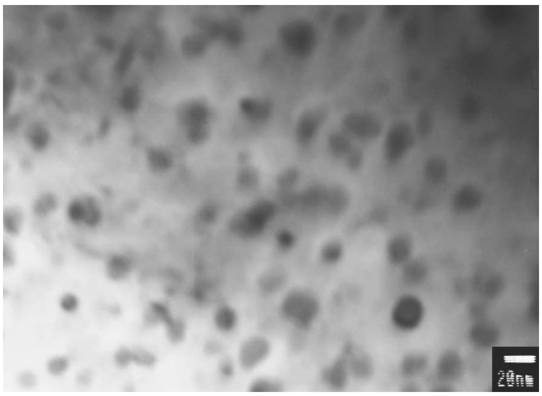
450°C/60 min



450°C/60 min



600°C/60 min



600°C/60 min

Fig. 30. Microstructure of CuTi4 alloy supersaturated, cold deformed with 50% reduction and aged at a temperature of 450°C and 600°C for 60 min. During the studies a strong influence of cold deformation after supersaturation on kinetics of the processes taking place during ageing. For comparison, Fig. 31 shows TTT diagram for the extent of reaction y = 0.6321

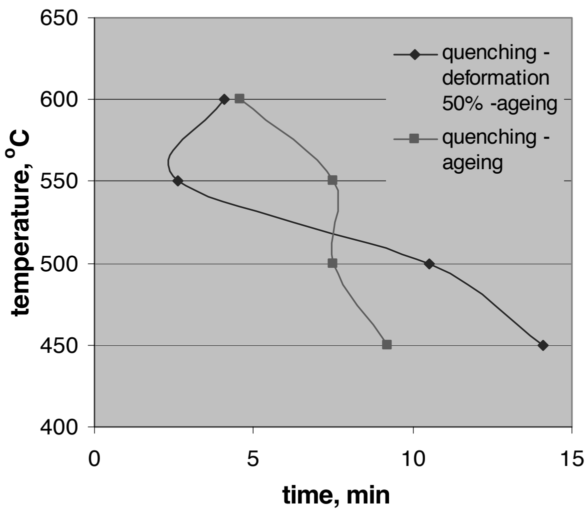


Fig. 31. TTT diagram for CuTi4 alloy after supersaturation and ageing, and after supersaturation, cold deformation (50% reduction) and for the extent of reaction y = 0.6321

6. Discussion

The results of the investigations into CuTi4 alloy widely confirmed the results of the studies presented by Dutkiewicz [5-8], who examined alloys of various titanium contents [5]: CuTi1.39; CuTi2.42; CuTi3.00; CuTi4.29 and CuTi5.50. The alloys were produced by melting and casting in an induction vacuum furnace. The ingots were subjected to homogenizing annealing at a temperature of 880°C for 5 hours in argon atmosphere. After annealing the ingots were rolled down to produce thin plates (thickness about 0.8 mm). The Cu-Ti alloys for supersaturation were held at a temperature of 900°C for 45 minutes and then quenched in water with ice. Ageing of all examined alloys was done at a temperature of 400 and 600°C in the periods from 15 minutes to over 30 days. Simultaneously conducted examinations of hardness showed that during ageing at a temperature of 400°C all the examined alloys reach their maximum hardness after about 15 days. Then the hardness does not change even after several months of further ageing. Increase of titanium content in the alloy from 1.39 to 4.29% resulted in increase of Brinell hardness from HB180 to HB240. Further increase of titanium content to 5.50% does not bring any hardness increase.

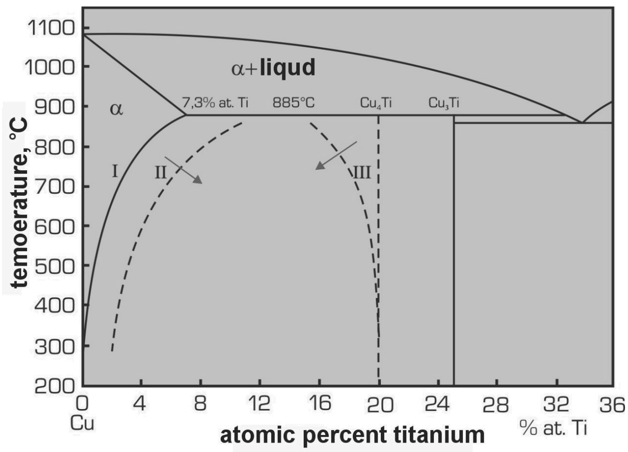


Fig. 32. Part of Cu-Ti equilibrium phase diagram; area I ̃ phase α, solid solution Ti in Cu; area II ̃ spinodal transformation curve; calculated with thermodynamical properties corrected by changeable solubility of Cu_4Ti; area III ̃ presence of metastable Cu_4Ti phase and hypothetical change of its solubility (III) [5]

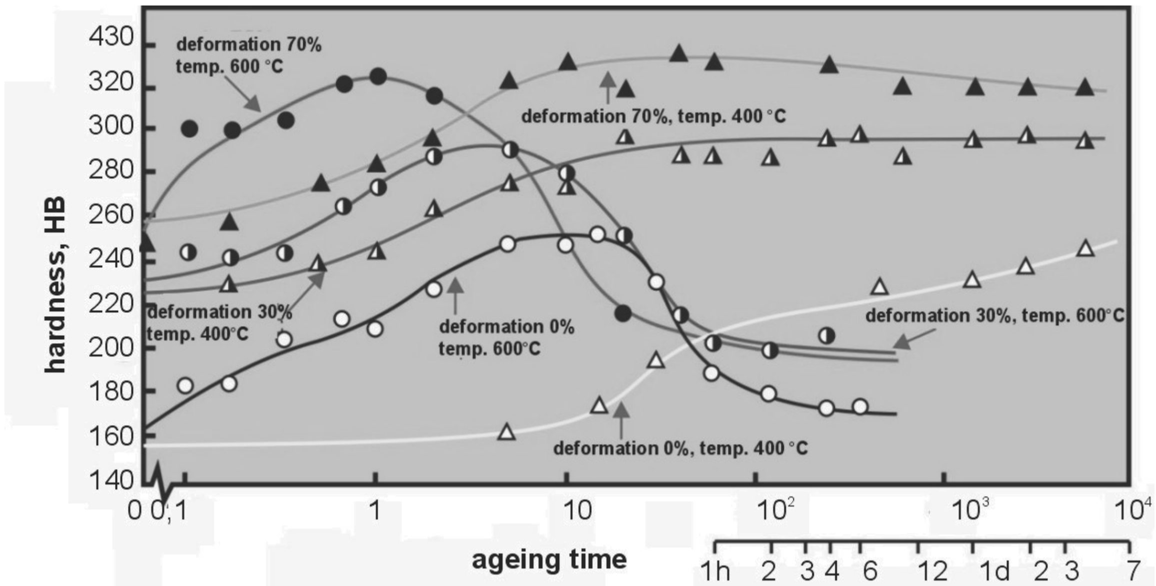


Fig. 33. Hardness of CuTi4.29 alloy after supersaturation versus ageing temperature, cold deformation and ageing time [5]

Examination of microstructure of Cu-Ti alloys in the assumed ageing conditions resulted in a conclusion that in the initial stages of their ageing (internal area of Fig. 32) a modulated microstructure is created which confirms spontaneity of the transition [5]. Additionally, in the microstructure of Cu-Ti alloys which were aged at a temperature of 400^0C ordered domains were observed.

The effects of generation of modulations and ordered structure during ageing of the supersaturated Cu-Ti alloys were accompanied with discrete precipitation at the grain boundaries. The discrete precipitates, of early forming nuclei, have negative influence on plastic properties of Cu-Ti alloy. The growth of precipitates takes place by migration of small angle boundary because of a higher diffusion rate along its course. The amount of discrete precipitates rapidly increases with ageing time.

The CuTi4.29 alloy deformed after supersaturation with 70% reduction and aged at a temperature of 600°C reaches its maximum hardness HB325 after 1 minute of ageing, and after 4 minutes if deformed with 30% reduction. The hardness of CuTi4.29 alloy decreases with increase of ageing time at a temperature of 600°C, both in the cold deformed after supersaturation alloy and in the not deformed one (Fig. 33). The reason for that is the simultaneous recrystallization and heterogeneous nucleation of stable phases in dislocations which eliminate the effect of hardening produced during ageing process.

The results of our studies also coincide with discussion by Bzowski and Gorczyca [9] who had established that spinoidal decomposition and continuous order in Cu-Ti alloys are observed at the same time. However, especially in the initial period, one of the processes has to precede the other one. On that basis two groups of binary alloys can be distinguished in which both processes are present. In the alloys of the first group (e.g. Cu-Ti) in the beginning spinoidal decomposition takes place and then the areas rich in one of the elements become ordered. In the second group (e.g. Cu-Be) the order of transformations is opposite. It has been shown that during ageing of Cu-Ti alloys a modulated structure is generated. Changes in chemical composition have no sinusoidal character. Discrete transition leads to formation of precipitates of Cu_3Ti equilibrium phase in a shape of lamellae layered alternatively with lamellae of solid solution. Periodically arranged in the matrix coherent precipitates are generated in the result of spinoidal transformation. Microstructure and chemical composition of equilibrium phase were not explicitly determined. Two types of equilibrium phase were defined: high-temperature disordered phase β` and low-temperature ordered phase β. The phase β` crystallizes in orthorhombic lattice of characteristic lattice constants:

$$a = 0.2572 – 0.2585 \text{ nm},$$
$$b = 0.4503 – 0.4527 \text{ nm},$$
$$c = 0.4313 – 0.4351 \text{ nm}.$$

The value of lattice constants of phase β` formed a basis for determination of titanium content: from 21 to 25 at%, which was assigned stoichiometric formula Cu_3Ti; the lattice constants obtained for titanium content of 25 at% correspond to the lattice constants of hexagonal structure A3 of compact lattice:

$$a = 0.262 \text{ nm},$$
$$b = 0.453 \text{ nm},$$
$$c = 0.427 \text{ nm}.$$

The results of microstructure examination were used to come up with a diagram of phase transitions in the aged Cu-Ti alloys (Fig. 34). Phase β crystallizes in orthorhombic structure of two times higher value of lattice constant *a* when compared to phase β` (Fig. 35).

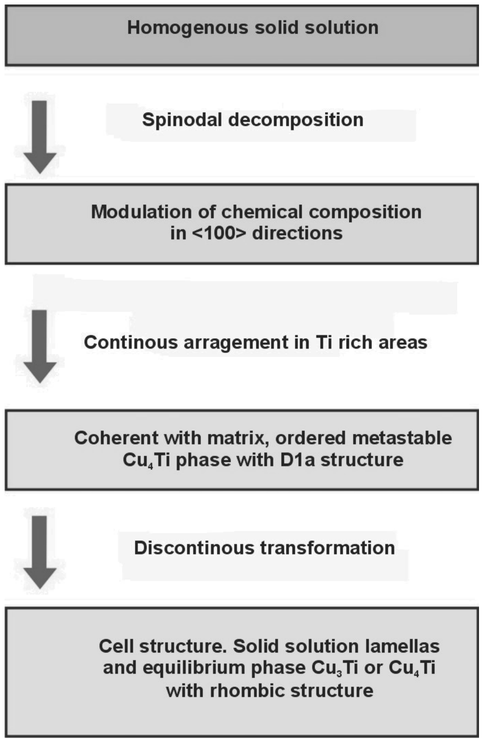


Fig. 34. Phase transitions in Cu-Ti alloys [9]

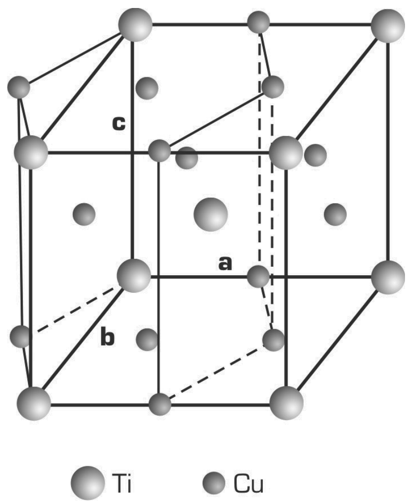


Fig. 35. Reciprocal orientation of unit cells of phase β` (hexagonal) and phase β (orthorhombic) [9]

Our studies were limited to cold deformation after supersaturation. Studies into precipitation in the conditions of high-temperature deformation of Cu-Ti alloys [10-21] present broader description of the phenomena and were carried out to determine influence of deformation and simultaneous decomposition of solid solution on the process of their hardening and microstructure. Especially structural changes which result from dynamic precipitation were considered. Błaż and Hameda [10-16] are of the opinion that the presence of substructure which is generated during high-temperature deformation accelerates precipitation by nucleation of precipitates on subgrains and dislocation tangles. Intensity of that nucleation can be competitive to the nucleation at the grain boundaries. The studies were conducted with the following alloys: CuTi1.46; CuTi3.5 and CuTi5. The alloys were held at a temperature of 900°C for 2 hours and quenched in water. The supersaturated alloys were deformed in the compression test with a constant deformation rate ($1.4x10^{-4}$ s^{-1}). The quenching time after high-temperature deformation is from 1 to 3 s. Observations of microstructure and analysis of the produced characteristics of high-temperature deformation of supersaturated Cu-Ti alloys provided grounds to distinguish four temperature ranges in which similar structural processes take place (Table 1).

Table 1.
Temperature ranges of high-temperature deformation of supersaturated Cu-Ti alloys resulting in production of similar characteristics microstructure [11]

Alloy	Range I °C	Range II °C	Range III °C	Range IV °C
CuTi1.46	400 - 600			≥ 700
CuTi3.5	400 – 500	600 – 700	700 – 750	≥ 800
CuTi5	400 - 500	600 - 750	750 - 800	≥ 900

Range I

In that deformation temperature range instability of compression test was observed. The yield stress reached its maximum then decreased. With further deformation also breaking of a sample can occur. The seeming softening of the material during deformation is related to localization of deformation and to the glide which leads to formation of shear bands as well as to formation of microcracks near grain boundaries. The increase of deformation temperature in that range resulted in homogenous nucleation and growth of precipitates of high dispersion degree. The increase of alloy hardening was facilitated by exceptionally high heterogeneity of deformation and formation of shear bands with no visible effects of matrix deformation outside the bands.

Range II

Process of heterogeneous deformation interacts with the process of discrete precipitation. It results in intensive growth and coagulation of Cu_3Ti phase precipitates in the bands of localized deformation. The structural changes manifest themselves by the maximum of yield stress which precedes the range of intensive softening of material during deformation.

Range III

Process of discrete transformation during heating up and stabilization of temperature before compression test results in a change of morphology of alloy microstructure. The deformation process runs virtually in a uniform way. Microstructure of the deformed alloy is characterized by presence of precipitates generated in the process of cellular growth and individual precipitates of elongated shape. Deformation curves $\sigma - \varepsilon$ in that temperature range run in a way which is characteristic for the materials undergoing dynamic recovery. After short range of hardening a range of plastic flow is observed at constant or slightly decreasing stress.

Range IV

Mechanical and structural effects of dynamic recrystallization were observed above the *solvus* temperature (yield stress maximum on deformation curve $\sigma - \varepsilon$, and then a decrease of yield stress and transition to the range of steady plastic flow with simultaneous nucleation and growth of new grains in the result of recrystallization).

Morphology of shear bands which are created in the Range II suggests possibilities of deformation by mechanical twinning [11,16]. Analysis of diffraction patterns of matrix and shear bands does not confirm twin orientation of the band with respect to the matrix. Localization of deformation is combined with a collective glide of large number of dislocations in the result of operation of stress concentrators in the strongly hardened matrix. Especially in the Range III, where discrete precipitation predominates, smaller precipitates in the bands of localized deformation become sheared in the result of strong deformation in the band.

Reduction of the efficient diameter of a precipitate results in its dissolving and simultaneous growth of other precipitates. In the conditions of diffusion, which is facilitated by high density of dislocations, it can lead to relatively fast growth of precipitates. The average diameter of precipitates created in the conditions of localized deformation is several times higher than of precipitates created in the result of cellular growth.

The decrease of precipitation hardening in the bands leads to further localized plastic flow in the bands and limitation of possibilities for deformation of the rest of the matrix hardened with precipitates of high dispersion. Growth of quasi-equiaxial precipitates in the bands of localized flow was defined as „*dynamic growth of precipitates*". Production of similar morphology of precipitates in static conditions is practically impossible.

Overageing of Cu-Ti alloys (decrease in hardness) during static ageing is attributed to the discrete transition and to the effects of cellular growth of precipitates. They substitute the volume of the material hardened in the initial stage of ageing with precipitates of high dispersion. In the conditions of strong localization of deformation the alloy matrix undergoes static ageing outside the plastic flow zone. In the zone of localized plastic flow, however, the rate of static structural changes related to overageing of the matrix is lower than in dynamic conditions.

The presented data and discussion show that examination of commercial CuTi4 alloy provides additional information on changes in microstructure and properties of the produced and processed alloy. It especially concerns the microstructure in a supersaturated state. In the microstructure of the supersaturated commercial CuTi4 alloy undissolved original particles of Ti are present as well as heterogeneous dissolving of titanium in copper matrix is observed. Also higher (when compared to laboratory alloys) level of impurities has a certain influence on the produced functional properties of the alloy. It especially affects mechanism and kinetics of precipitation and, in consequence, results of hardening and recrystallization process. Not complete dissolving of the alloying component compromises the effects of precipitation hardening while the level of impurities and primary precipitates of undissolved Ti particles result in increase of recrystallization temperature.

7. Conclusions

Studies into microstructure and properties of commercial CuTi4 alloy with special consideration for mechanism and kinetics of precipitation were conducted. Basing on the results and discussion it was established that:

- Decomposition of supersaturated solid solution in that alloy is similar to the alloys produced in laboratory scale. The observed differences in microstructure after supersaturation were related to the presence of undissolved Ti particles and increased segregation of titanium distribution in copper matrix including microareas of individual grains.
- The above mentioned factors influence the mechanism and kinetics of precipitation and subsequently the produced wide ranges of functional properties of the alloy.
- Cold deformation (50% reduction) of the alloy after supersaturation changes the mechanism and kinetics of precipitation and provides possibilities for production of broader sets of functional properties. It is expected that widening of the cold deformation range should result in more complete characteristics of material properties, suitable for the foreseen applications. Similar effects can be expected after application of cold deformation after ageing.

The elaborated research results present some utilitarian qualities since they can be used in development of process conditions for industrial scale production of strips from CuTi4 alloy of defined properties and operating qualities.

Acknowledgements

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Additional information

Selected issues related to this paper are planned to be presented at the 16th International Scientific Conference on Contemporary Achievements in Mechanics, Manufacturing and Materials Science CAM3S'2010 celebrating 65 years of the tradition of Materials Engineering in Silesia, Poland and the 13th International Symposium Materials IMSP'2010, Denizli, Turkey.

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