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Misorientation in rolled CuTi4 alloy

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ABSTRACT

Purpose: The aim of the work is to investigate the microstructure heat treated and cold rolled commercial copper alloy CuTi4.

Design/methodology/approach: The Investigations of the structure were made on ZEISS SUPRA 25 with EBSD method. Observations of the structure on thin foils were made on the JOEL 3010 transmission electron microscope (TEM).

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; Electron microscopy; Heat treatment; CuTi4 alloy

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MATERIALS

1. Introduction

Copper alloys composes with different elements and improvement of production technology which create new possibilities in the technical demand. Nowadays, they are widely applied and most commonly used alloys in the group of non-ferrous metals [1-9]. Copper-base alloys are widely used for the applications due to high strength as well as good electrical conductivity. Copper alloys are usually of the precipitation strengthened types and are dilutely alloyed with elements of very low solubility to preserve high levels of conductivity.

Mechanical properties of copper are improved (apart from cold working) by a small addition - of up to 3% - of alloying elements which, however, reduce the electrical conductivity to a different extent. These alloys are traditionally named high-alloyed coppers. The semi-finished products from this group are characteristic of the high and stable mechanical properties at the elevated operating temperatures, and also of the good electrical and thermal conductivity.

Copper alloys with addition of beryllium called traditionally the beryllium copper [10] which, apart from their high toxicity and technological problems with its fabricating and processing [11], are widely used because of their advantageous mechanical properties, as well as their corrosion - and abrasion wear resistance. One of the most important advantages of these alloys is that they have no susceptibility to sparking. This advantage predestines the CuBe alloys for use in constructional elements of tools and equipment designed for operation in explosive conditions (mines, engine rooms, etc.) [12]. Works on CuTi alloys are the effect of search for the CuBe alloys' substitutes. The CuTi alloys compared to the beryllium copper are characteristic of the similar electrical properties and comparable mechanical ones. The most effective way to improve the strength properties of the CuTi alloys is their precipitation hardening connected with strain hardening. Therefore, the intensive investigation is ongoing of the effect of the joint (alternate) heat treatment and plastic working, or heat treatment with cold working between the supersaturation- and ageing operations and after ageing [13-15]. It is worthwhile to mention that the spinodal transformation is of crucial importance here.

As the research results to date indicate [16-19] alloys containing 2-6% Ti are most promising because of their potential applications first of all in the power- and electronic industry branches [19,20] and for the equipment elements for the mine rescue units and anti-terrorist squads [21]. Research is also carried out on forming the microstructure and also on improving the mechanical- and physical properties of CuTi alloys by introducing the alloying elements [22-25].

The goal of this work was to determine the ageing time effect on microstructure and properties of CuTi4 alloy cold worked by rolling with the 50% total reduction after supersaturation and next aged at temperature of 550°C for 1 min, 60 min, and 420 minutes.

2. Material and methods

Investigations were carried out on the commercially available CuTi4 alloy. Chemical composition of the industrial CuTi4 alloy is presented in Table 1.

Table 1.
Chemical composition of CuTi4 alloy

Cu	Ti	Zn	P	Pb	Sn	Mn	Ni	Sb	Bi	As	Cd
95.83	3.95	0.13	0.065	0.003	0.009	0.030	0.01	0.001	0.001	0.001	0.001

The material preparation procedure for investigation of CuTi4 alloy included:

- hot working with 80% draft to 3.0 mm thickness,
- supersaturation (920°C/1h) in water,
- cold working with 50% draft,
- ageing at temperature of 550°C for 1 min, 60 min, and 420 minutes.

Examinations of microstructure and grains misorientation were made on ZEISS SUPRA 25 scanning electron microscope using the EBSD method and with JEOL 3010 transmission electron microscope.

X-ray phase analysis of the specimens was made on Panalytical X'Pert diffractometer using filtered radiation of the lamp with cobalt anode. The measurement step was 0.05° and the impulse counting time was 10 sec.

3. Results and discussion

The maximum solubility of titanium in copper at the temperature of 885°C is 8% at. (Fig. 1). The metastable intermediate phases with the ordered structure may originate before precipitation of the equilibrium $\beta TiCu_4$ phase. The peritectic reactions occurring between the melting point of the TiCu phase particles and the eutectic transformation temperature lead to origination of the Ti_3Cu_4, Ti_2Cu_3, $TiCu_2$, and $TiCu_4$ intermetallic phases. Moreover, two equilibrium $TiCu_4$ phases occur in CuTi alloys - stable β and metastable α. The α. phase is transformed into β phase after long ageing (even at low temperature). Probably transformation is possible of β phase during cooling into the α one stable at low temperature [11,26].

The electron microscopy methods made the detailed phase components analysis possible of the CuTi4 alloy microstructure after its complex heat- and mechanical treatment composed of:

hot working → supersaturation → cold working → ageing

Ageing of the supersaturated CuTi alloy containing about 4% T at. induces the spinodal decomposition accompanying precipitation of phases with the unordered structure, alternatingly enriched and impoverished with Ti.

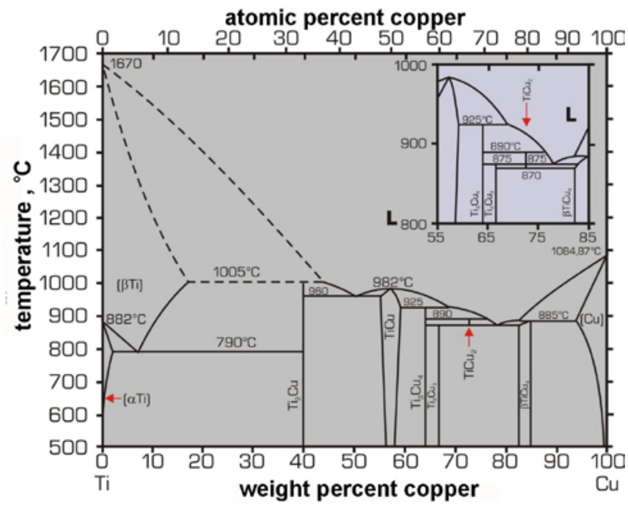

Fig. 1. Ti-Cu phase equilibrium system [27]

Investigation results presented by Dutkiewicz [28-31] revealed that extension of the CuTi4 alloy ageing time leads to dissolving the precipitated particles of the second phase, which results with reduction of the alloy hardness.

As a result of the discontinuous transformation the Cu_3Ti equilibrium phase lamellae originate arranged alternately with the solid solution lamellae. The coherent precipitations originating as a result of the spinodal transformation are arranged periodically. Chemical composition and microstructure of the equilibrium phase are not unambiguously defined. Two types of the equilibrium phases are distinguished:

- the unordered, high-temperature β`phase,
- the ordered, low-temperature β phase.

The β` phase crystallizes in the hexagonal lattice, whereas the β phase in the rhomb lattice [13,14].

In metals with the A1 regular lattice, like copper, the dynamic recrystallization usually does not occur in the hot working process. The grainy structure of metal originates in this case as a result of re-polygonization and coalescence of subgrains with participation of dislocation climb. The grain size is described with the relationship [32] then:

$$d^{-1} = A + B\log Z \qquad (1)$$

where:
A and B - constants,

$Z = \dot{\varepsilon}\exp(\frac{Q}{RT})$ - Zener-Hollomon parameter,
where:
Q - process activation energy,
R - gas constant,
T - absolute temperature.

Supersaturation occurring next causes dissolving the phases in matrix (except the primary precipitations) and also the average grain size growth and deterioration of the mechanical properties connected with it.

Material strengthening by structure refinement, inducing, and cumulation of the point - and line defects of the crystal lattice occurs during the next process stage - cold working with 50% reduction.

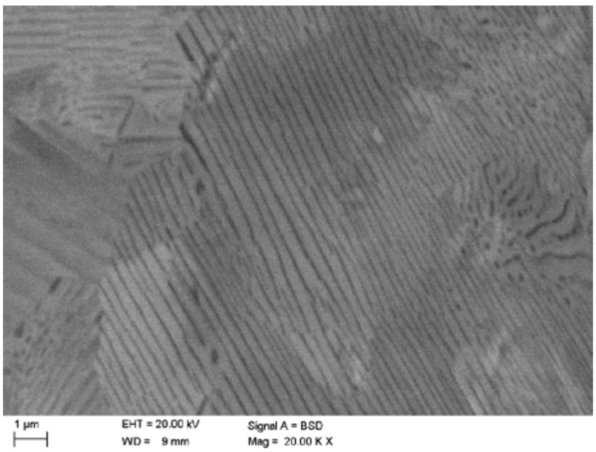

Fig. 2. Microstructure of CuTi4 alloy aged at temperature of 550°C for 420 minutes, visible laminar precipitations; SEM

It was confirmed, based on investigation results, that during the last treatment phase - ageing - spinodal decomposition occurred in the alloy (Figs. 2 and 3). This mechanism, along with the accompanying structure changes, occurs in three particular cases [33]. The first one occurs in alloys aged in the 600-900°C temperature range for 100 hours, which were not deformed before. Next, the spinodal decomposition and continuous spinode precipitation take place in alloys which were previously deformed, aged at low temperature. The continuous precipitation extent (intensity) grows along with the ageing temperature rise. However, the spinodal decomposition, and continuous and discontinuous spinode precipitations take place in alloys which were previously deformed, aged at high temperature. The structure is non-homogeneous. Finally structure defects caused by deformation disappear [34-37].

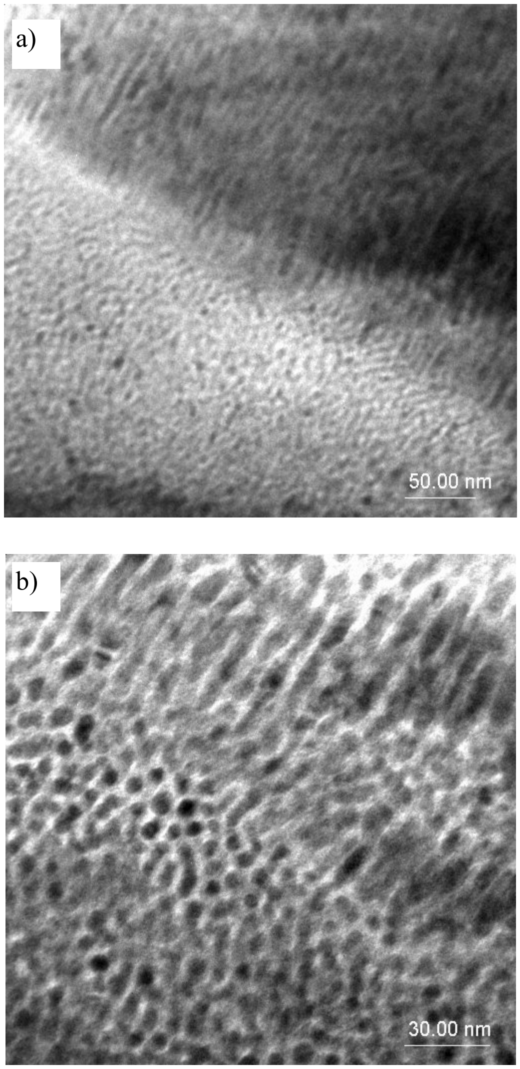

Fig. 3. Microstructure of CuTi4 alloy aged at temperature of 550°C for 1 minute, image in the light field, boundary between the continuous and discontinuous precipitations areas is visible, TEM

The spinode wave length may be evaluated using Daniel-Lipson's relationship [38], based on the qualitative X-ray phase analysis comparing the obtained X-ray diffraction patterns for various ageing duration [39, 40]:

$$\lambda = \frac{ha_0}{h^2 + k^2 + l^2} \times \frac{tg\theta_B}{\Delta\theta} \tag{2}$$

where:
h, k, l - Miller indices of the Bragg peak,
$\Delta\theta$ - difference of the Bragg peak maximum position,
θ_B - is the value of the Bragg angle,
a_0 - lattice cell parameter for the homogenized alloy.

Ageing time is of a big importance in forming the final microstructure. The measurement results revealed that the high-angle boundaries' portion in the investigated microstructure grows along with extending the ageing time, at the expense of the small-angle boundaries' portion. As it results from the EBSD analysis (Tables 2-4) of CuTi4 alloy hot worked alloy with 80% reduction, next supersaturated (920°C/1h) in water, cold worked with 50% reduction, and aged at temperature of 550°C for 1min, its small-angle (2-15°) boundaries' portion is above 61% in the investigated microstructure, while the remaining 39% are the high-angle (15-180°) boundaries. This attests to domination of fine grains in the microstructure, which originated due to cold plastic strain, and too short ageing time did not provide appropriate conditions for grain growth. On the other hand, the small-angle boundaries in the microstructure of the alloy aged finally at the temperature of 550°C for 420 min have only 10%, portion whereas the high-grained boundaries being the proof for grain growth have 90% share.

Portions of the small- and high-angled boundaries after ageing for 60 minutes are presented to illustrate this process. The wide-angle boundaries' portion is above 72%. This attests the fact that in the investigated CuTi4 alloy, after the alternate plastic strain and heat treatment, the highest growth of the high-angled grains portion occurs during the first ageing hour, later this portion does not grow that fast.

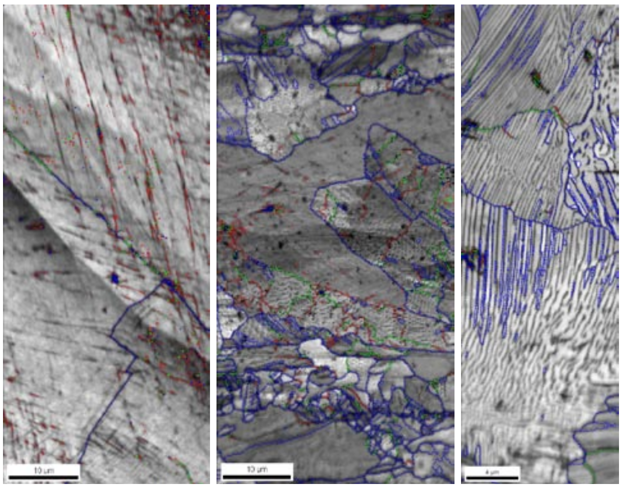

Fig. 4. Microstructure of CuTi4 alloy aged at temperature 550°C for a) 1 min, b) 60 min, c) 420 min; grains orientation maps using Euler angles - red and green lines - small-angle boundaries, blue lines - high-angle boundaries

Table 2.
CuTi4 alloy after supersaturation, 50% reduction, and ageing at the temperature of 550°C for 1 minute (Fig. 4a)

	min	max	Portion [%]	Number of boundaries	Total length [mm]
	3°	5°	43.9%	35489	10.9
	5°	15°	17.2%	13912	4.02
	15°	180°	38.9%	31479	9.09

Table 3.
CuTi4 alloy after supersaturation, 50% reduction, and ageing at the temperature of 550°C for 60 minutes

	min	max	Portion [%]	Number of boundaries	Total length [µm]
	2°	5°	14.9%	2051	355.24
	5°	15°	12.6%	1741	301.55
	15°	180°	72.5%	10018	1740

Table 4.
CuTi4 alloy after supersaturation, 50% reduction, and ageing at the temperature of 550°C for 420 minutes

	min	max	Portion [%]	Number of boundaries	Total length [µm]
	2°	5°	5.10%	618	35.68
	5°	15°	4.90%	464	26.79
	15°	180°	90.0%	10716	618.69

The small-angle boundaries, that is boundaries with the small misorientation angle, to which twinned boundaries are included, originate due to plastic strain (mechanical twins) and because of recrystallisation (annealing twins). The twinned boundaries developed because of the cold plastic strain - rolling (Fig. 5) preceded by ageing of the investigated alloys, whereas the annealing twins originated during ageing (Fig. 6).

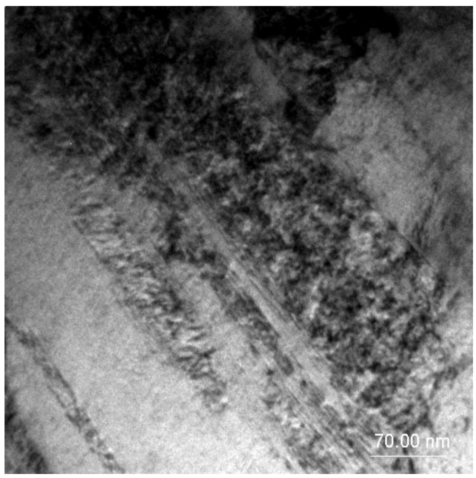

Fig. 5. Microstructure of CuTi4 alloy aged at temperature of 550°C for 1 minute, image in the bright field; TEM

As it turns out from Fig. 7a, microstructure of CuTi4 alloy aged at temperature of 550°C for 1 minute is characteristic of the big grain diameter - grains were not revealed with diameter smaller than 22 µm (Table 5). Moreover, compared to the microstructure obtained after 60 minutes (Fig. 7b) and after 420 minutes (Fig. 7c) of ageing, grains with sizes from the 22-35 µm range have 100% portion in the microstructure.

Next, in the microstructure of CuTi4 alloy aged for 60 or 420 minutes, grains with sizes of 0.22-8.8 µm have the biggest portions, 45.3 and 46% respectively (Table 6, Table 7). Moreover, grains with sizes from the 8.6-12.1 µm range have the significant portions in the microstructure, of 27.5 and 17.6% respectively. In total, grains with sizes of 0.22-19.2 µm, which were not observed after 1 minute of ageing, have 100% portion in both remaining cases. No bigger sized grains were revealed in the observed microstructure.

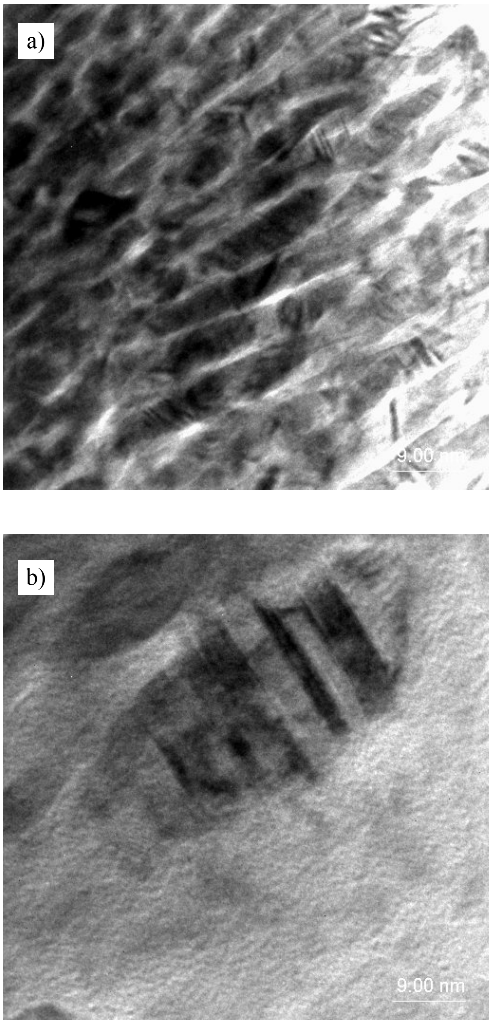

Fig. 6. Microstructure of CuTi4 alloy aged at temperature of 550°C for 1 minute; continuous precipitation lamella with the annealing twin visible; TEM

Nucleation of grains with sizes much smaller than those after 1 minute of ageing is connected undoubtedly with the ongoing primary recrystallisation process occurring in the solid solution without any changes of the initial phase and transformation product. Growth of the recrystallisation nuclei takes place by movement of the high-angle grain boundaries. Migration of the high-angle grain boundaries (Tables 2-4) is caused by the difference of atoms transitions through the energy barrier of the recrystallisation front G_m from the plastically deformed matrix to the growing nucleus and vice versa [41]. The atom undergoing transition from matrix with the high dislocation density to the recrystallised grain obtains the additional propelling force of a big value $F_r b^3$ (b^3 - atom volume) if the propelling force F_r acts on the recrystallisation front. Therefore, the recrystallisation front migration movement rate is:

$$v = b\nu_D c_v \left\{ \exp(-\frac{\Delta G_m}{kT}) - \exp[-\frac{\Delta G_m + F_r b^3}{kt} \right\} \tag{3}$$

where:
ν_D - Debye frequency equal to $10^{13} s^{-1}$,
c_v - concentration of vacancies at the grains boundary,
k - Boltzman constant,
T - temperature, K.

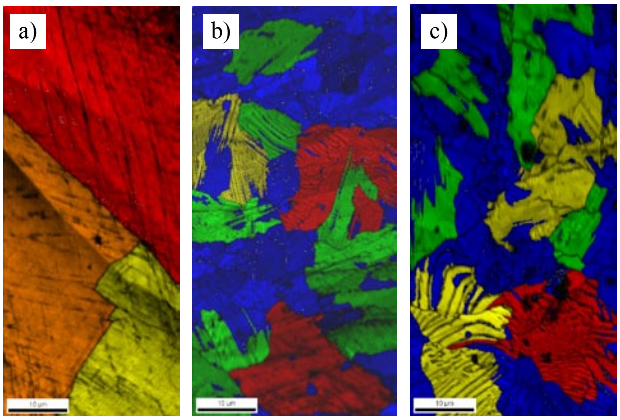

Fig. 7. Microstructure of CuTi4 alloy aged at temperature of 550°C for a) 1 min, b) 60 min, c) 420 min, grains size

Table 5.
CuTi4 alloy (supersaturated - cold worked), aged at 550°C for 1 min (Fig. 7a)

	Grain size [µm]		Portion [%]
	min	min	
	0.22	15.68	0
	15.68	22.18	0
	22.18	27.17	19.0
	27.17	31.37	34.8
	31.37	35.07	45.9

Table 6.
CuTi4 alloy (supersaturated - cold worked), aged at 550°C for 60 min (Fig. 7b)

	Grain size [µm]		Portion [%]
	min	min	
	0.29	8.61	45.3
	8.61	12.17	27.5
	12.17	14.91	5.1
	14.91	17.21	0
	17.21	19.24	21.5

Table 7.
CuTi4 alloy (supersaturated - cold worked), aged at 550°C for 420 min (Fig. 7c)

	Grain size [µm]		Portion [%]
	min	max.	
	0.222	8.54	46.0
	8.54	12.08	17.6
	12.08	14.80	23.5
	14.80	17.08	0.0
	17.08	19.10	11.6

Based on analysis of the pole figures (PF) images it was analysed how alignment of the crystal lattice cells in the neighbouring grains changes due to misorientation.

Misorientation between the base cells of the crystal lattice A and B (Fig. 8) is defined as rotation transforming the reference system of cell B into the reference system of cell A.

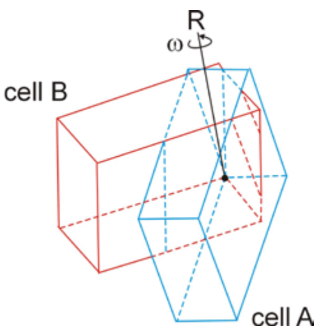

Fig. 8. Misorientation between cells [42]

Misorientation may be mathematically described in many ways:

- rotation angle / rotation axis pair,
- rotation matrix,
- Euler's angles,
- quaternions,
- Rodriguez's vectors.

$$K_A = \Gamma_{AB} \cdot K_B \tag{4}$$

$$\Gamma^e_{AB} = S_i \cdot \Gamma_{AB} \cdot P_j \tag{5}$$

where:
S_i and P_j are the elements of symmetry of the first and second crystallite respectively (i=1, …, M, j=1, …, N).

Areas of the same colour in the presented figures (Fig. 9), represent the region in which the consistent orientation of the crystal lattice cells is present. In the region, in which the clear boundary (line) is visible between areas with the different colours misorientation of the crystal lattice occurs. Based on these observations one may also notice the significant inhomogeneity of the microstructure refinement (Fig. 9b).

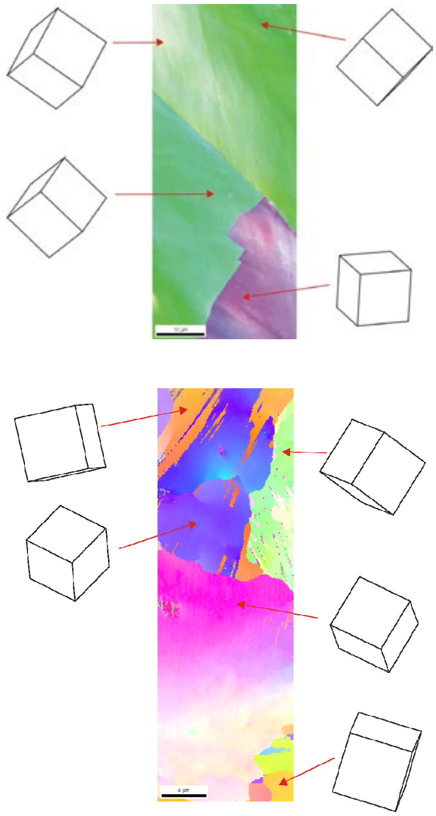

Fig. 9. Grains misorientation in CuTi4 alloy microstructure, aged at temperature of 550°Cfor: a) 1 min, b) 420 min;

Defining the mutual orientation of grains (misorientation) is useful during investigation of the plastic strain mechanisms (passing the slip from grain to grain), of twinning phenomenon (mutual orientation of twins) or during examination of structure of grains boundaries.

4. Conclusions

It was found, based in microstructure analysis with EBSD, that along with the ageing time of CuTi4 alloy, the portion of the small-angle boundaries from the range of 2-15° gets smaller, being for 1, 60, and 420 minutes of ageing equal to 61.1, 26.5, and 9.1% respectively, whereas the portion of the high-angle boundaries from the range of 5-180° grows, being for 1, 60, and 420 minutes of ageing equal to 38.9, 72.5, and 90.9% respectively. Growth of the high-angle boundaries' portion attests irrefutably to movement of the high-angle boundaries, i.e., to the grain growth. As the precisely defined direction of the boundary movement (towards the centre of its curvature) makes the grain growth selective, then grains with number of sides bigger than six grow, and grains with the umber of sides smaller than six are on the wane. Simultaneous reduction of the small-angle boundaries portion attests to the dominating grain growth process.

Investigation of structure with the EBSD method of the CuTi4 alloy hot worked with 80% reduction, supersaturated next (920°C/1h) in water, next cold worked with 50% reduction and aged at the temperature of 550°C for 1, 60, and 420 minutes, made it possible to examine in detail of the ageing time on the development extent of the small- and high-angle grain boundaries, and to examine the grains disintegration extent in the investigated microstructure. One may observe the clear growth of the high-angle grain boundaries portion, whose intensity accumulates in the first hour of ageing. Moreover, based on observation of the microstructure, the significant inhomogeneity of the refinement extent was noticed, and one may suppose also that the cold plastic strain energy was used for reorganisation of the high-angle grains.

The structural phenomena occurring during heat treatment of the cold worked metals and alloys do not allow to separate recovery from recrystallisation [43]. However, as the continuous recrystallisation process proceeds without movement of the high-angle grains boundaries, one may infer , based on the obtained results that in the ageing process at the temperature of 550°C/420 minutes, recovery and grains growth are the dominating mechanism.

Moreover, results of the grains size measurement using EBSD indicate how difficult it is to separate the recovery process from recrystallisation . It turns out from them that apart from growth of the high-angle boundaries portion along with extension of the ageing time, the process of nucleation of the new grains of very small size takes place, which in turn is the proof for the recrystallisation process taking place simultaneously.

References

[1] W. Ozgowicz, W. Malec, L. Ciura, Investigation on the deformability of tin bronzes CuSn6 modified with zirconium on the industrial hot rolling of flat ingots, Journal of Achievements in Materials and Manufacturing Engineering 24/1 (2007) 78-83.

[2] W. Ozgowicz, E. Kalinowska-Ozgowicz, B. Grzegorczyk, The microstructure and mechanical properties of the alloy CuZn30 after recrystallizion annealing, Journal of Achievements in Materials and Manufacturing Engineering 40/1 (2010) 15-24.

[3] T. Küçükömeroğlu, G. Pürçek, O. Saray, L. Kara, Investigation of friction and wear behaviours of CuSn10 alloy in vacuum, Journal of Achievements in Materials and Manufacturing Engineering 30/2 (2008) 172-176.

[4] S. Özdemir Kart, A. Erbay, H. Kılıç, T. Cagin, M. Tomak, Molecular dynamics study of Cu-Pd ordered alloys, Journal of Achievements in Materials and Manufacturing Engineering 31/1 (2008) 41-46.

[5] A.O. Olofinjanaa, K.S. Tan, Achieving combined high strength and high conductivity in re-processed Cu-Cr alloy, Journal of Achievements in Materials and Manufacturing Engineering 35/1 (2009) 14-20.

[6] W. Ozgowicz, B. Grzegorczyk, The influence of the temperature of plastic deformation on the structure and mechanical properties of copper alloys CuCo2Be and CuCo1Ni1Be, Archives of Materials Science and Engineering 39/1 (2009) 5-12.

[7] G. Wnuk, M. Zielińska, Microstructural and thermal analysis of Cu-Ni-Sn-Zn alloys by means of SEM and DSC techniques, Archives of Materials Science and Engineering 40/1 (2009) 27-32.

[8] B. Leszczyńska-Madej, M. Richert, Microstructure and properties of dynamically compressed copper Cu99.99, Journal of Achievements in Materials and Manufacturing Engineering 39/1 (2010) 35-42.

[9] B. Oleksiak, G. Siwiec, A. Blacha, J. Lipart, Influence of iron on the surface tension of copper, Archives of Materials Science and Engineering 44/1 (2010) 39-42.

[10] L.A. Dobrzański, metal engineering materials, WNT, Warsaw, 2004.

[11] Z. Rdzawski, Low alloyed copper, Silesian University of Technology Publishing House, Gliwice, 2009.

[12] Z. Rdzawski, W. Głuchowski, Mechanism of decomposition CuBe supersaturated alloy, The Ores and Non-ferrous Metals R 54/3 (2009) 143-148.

[13] S. Nagarjuna, M. Srinivas, Grain refinement during high temperature tensil testing of prior cold worked and peak aged Cu-Ti alloys: Evidence of superplasticity, Materials Science and Engineering A 498 (2008) 468-474.

[14] S. Nagarjuna, U. Chinta Babu, Partha Ghosal, Effect of cryo-rolling on age hardening of Cu-1.5Ti alloy, Materials Science and Engineering A 491 (2008) 331-337.

[15] Z. Rdzawski, J. Stobrawa, W. Głuchowski, J. Konieczny, Thermomechanical processing of CuTi4 alloy, Journal of Achievements in Materials and Manufacturing Engineering 42/1-2 (2010) 9-25.

[16] S. Nagarjuna and D.S. Sarma, On the variation of lattice parameter of Cu solid solution with solute content in Cu-Ti alloys, Scripta Materialia 41/4 (1999) 359-363.

[17] S. Nagarjuna, M. Srinivas, K. Balasubramanian, D.S. Sarma, On the deformation characteristic of solution treated Cu-Ti alloys, Scripta Metallurgica et. Materialia 33/9 (1995) 1455-1460.

[18] S. Nagarjuna, M. Srinivas, K. Balasubramanian, D.S. Sarma, Effect of modulations on yield stress and strain hardening exponent of solution treated Cu-Ti alloys, Scripta Materialia 38/9 (1998) 1469-1474.

[19] S. Nagarjuna, M. Srinivas, High temperature tensile behaviour of a Cu-1.5 wt.% Ti alloy, Materials Science and Engineering A 335 (2002) 89-93.

[20] S. Nagarjuna, K. Balasubramanian, D.S. Sarma, Effect of prior cold work on mechanical properties, electrical conductivity and microstructure of aged Cu-Ti alloys, Journal of Materials Science 34 (1999) 2929-2942.

[21] L. Blacha, G. Siwiec, A. Kościelna, A. Dudzik-Truś, Influence of titanium contents on microstructure and properties Cu-Ti system alloys, Materials Engineering 6 (2009) 520-524 (in Polish).

[22] R. Markandeya, S. Nagarjuna, D. S. Sarma, Effect of priori cold work on age hardening of Cu-4Ti-1Cr alloy, Materials Science and Engineering A 404 (2005) 305-313.

[23] T.J. Konno, R. Nishio, S. Semboshi, T. Ohsuna, E. Okunishi, Aging behavior of Cu-Ti-Al alloy observed by transmission electron microscopy, J Master. Science 43 (2008) 3761-3768.
[24] S. Nagarjuna, D. S. Sarma, Effect of cobalt additions on the age hardening of Cu-4.5Ti alloy, Journal of Materials Science 37 (2002) 1929-1940.
[25] R. Markandeya, S. Nagarjuna, D.S. Sarma, Precipitation hardening of Cu-3Ti-1Cd alloy, Journal of Materials Engineering and Performance 16 (2007) 640-646.
[26] P. Canale, C. Servant, Thermodynamic assessment of the Cu-Ti system taking into account the new stable phase $CuTi_3$, International Journal of Materials Research 93 (2002) 273-276.
[27] T.B. Massalski, Binary alloys phase diagrams 7th Edition, ASM International, Ohio, 1990.
[28] J. Dutkiewicz, Mechanism of spinodal and dicscountinous decomposition and ordering processes in aged alloys with A1 structure, Metallurgy and Foundry 80 (1977).
[29] J. Dutkiewicz, L. Lityńska, Rusing of elektron diffraction for investigation of spinodal decomposition in Cu-Ti and Al-Zn alloys, Proceedings of the 5th Conference "Electron Microscopy of Solids", Warsaw-Jadwisin, 1978, 149-154.
[30] J. Dutkiewicz, Spinodal decomosition, ordering and discontinous precipitation in deformed and aged copper-titanium alloys, Metals Technology, October (1978) 333-340.
[31] J. Dutkiewicz, L. Lityńska, Ordering within percipitates in copper-nickel-titanium alloys, Journal of Materials Science 15 (1980) 2307-2310.
[32] G. Gottstein, Rekristallisation metallischer werkstoffe, DMG, 1984.
[33] H.X. Li, X.J. Hao, G. Zhao, S.M. Hao, Characteristics of the continuous coarsening and discontinuous coarsening of spinodally decomposed Cu-Ni-Fe alloy, Journal of Materials Science 36 (2001) 779-784.
[34] J.-C. Zhao, M.R. Notis, Spinodal decomposition, ordering transformation, and discontinuous precipitation in a Cu-15Ni-8Sn alloy, Acta Materialia 46/12 (1998) 4203-4218.
[35] M.A. Mangan, G.J. Shiflet, Tree dimensional investigation of CuTi discontinuous precipitation, Scripta Meterialia 37/4 (1997) 517-522.
[36] I.K. Razumov, Formation of intermediate ordered states on spinodal decomposition of alloys, Journal of Engineering Physics and Thermophysics 81/4 (2008) 826-833.
[37] V. Sofonea, K.R. Mecke, Morphological characterization of spinodal decomposition kinetic, The European Physical Journal B 8 (1999) 99-112.
[38] V. Daniel, H. Lipson, An X-ray study of the dissociation of an alloy of copper, iron and nickel, Proceedings of the Royal Society London A 181/987 (1943) 368-378.
[39] V. Lebreton, D. Pachoutinski, Y. Bienvenu, An investigation of microstructure and mechanical properties in Cu-Ti-Sn alloys rich in copper, Materials Science and Engineering A 508 (2009) 83-92.
[40] P. Prasad Rao, B.K. Agrawal, A.M. Rao, Comparative study of spinodal decomposition in symmetric and asymmetric Cu-Ni-Cr alloys, Journal of Materials Science 26 (1991) 1485-1496.
[41] J. Adamczyk, Theoretical metal science, Part 2, Plastic deformation, consolidation and cracking, Publishing House of Silesian University of Technology, Gliwice, 2005.
[42] K. Sztwiertnia, M. Faryna, G. Sawina, Quantitative misorientation characteristics in interphase boundaries in composites, Journal of Microscopy 224 (2006) 4-7.
[43] M. Blicharski, S. Gorczyca, Recrystallization with participation of second phase, The Library of Physics Metals, Publishing House Śląsk, Katowice, 1980 (in Polish).