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FORMATION OF MICROSTRUCTURE AND PROPERTIES OF Cu-3Ti ALLOY IN THERMAL AND THERMOMECHANICAL PROCESSES

This paper presents the possibilities of forming the microstructure as well as mechanical properties and electrical conductivity of Cu-3Ti alloy (wt.%) in thermal and thermomechanical processes that are a combination of homogenising treatment, hot and cold working, solution treatment and ageing. Phase composition of the alloy following various stages of processing it into the specified semi-finished product was being determined too. It was demonstrated that the application of cold plastic deformation between solution treatment and ageing could significantly enhance the effect of hardening of the Cu-3Ti alloy without deteriorating its electrical conductivity. It was found that for the investigated alloy the selection of appropriate conditions for homogenising treatment, hot and cold deformation as well as solution treatment and ageing enables to obtain the properties comparable to those of beryllium bronzes.

Keywords: Copper-titanium alloy, microstructure, thermal and thermomechanical processes

1. Introduction

The precipitation hardened Cu-Be alloys, called beryllium bronzes, are characterised by the highest mechanical properties among copper alloys, very good corrosion and abrasion resistance, high electrical and thermal conductivity, and the lack of inclination to sparking [1-2]. Their strong toxicity caused that their use has been banned in Poland and EU countries for many years [3]. The research, conducted for many years all over the world, focused on finding non-toxic substitutes for beryllium bronzes have shown that these can be Cu-Ti binary alloys or Cu-Ti-X complex alloys, called titanium bronzes [1,2,4-7].

Titanium bronzes are usually melted in induction furnaces, more rarely in electric arc furnaces with nonconsumable electrode or plasma melting furnaces [4, 6-10]. In the melting process, very clean charge materials in the form of oxygen-free electrolytic copper with a purity of 99.99% and Cu-Ti master alloy are used [4,6,7]. The melting process is carried out in water-cooled corundum, magnesite, graphite-yttrium or metal crucibles [8,11]. Liquid alloys are most often cast into graphite moulds and cooled in the furnace chamber under vacuum. After crystallisation, they are subjected to long-term homogenising treatments at high temperature.

Titanium bronzes are rarely used in the as-cast condition and are usually plastically worked by forging or hot rolling or cold rolling, drawing and extrusion [6,7,12,13].

Due to variable titanium solubility in copper [5-7], titanium bronzes are subjected to the final heat treatment consisting of precipitation hardening or thermomechanical treatment and ageing. The solution treatment of titanium bronzes is usually carried out from approx. 900°C. The effect of the solution treatment is the dissolution of small precipitates of intermetallic phases formed by Cu and Ti that have remained in the microstructure after homogenising treatment. The ageing is carried out at 400÷600°C for up to several hours. This allows to achieve strength properties and electrical conductivity that are comparable to those obtained for Cu-Be alloys [5,14,15]. The use of thermomechanical treatment and ageing enables to obtain higher strength properties. The cold deformation between solution treatment and ageing allows to have much higher hardening after a shorter ageing time compared to alloys subjected to solution treatment and ageing only [15,16].

The aim of this paper was to evaluate the possibilities of formation of the microstructure and selected properties of Cu-3Ti alloy in thermal and thermomechanical processes consisting of different combinations of heat treatment with hot and cold working. As a consequence it will be the development of the processing technology basis of this alloy and other titanium bronzes into various semi-finished and finished products.

2. Experimental procedure

The material for investigations was Cu-Ti alloy containing approx. 3.0 wt.% Ti (2.8% according to the ladle chemical analysis). The alloy was melted in a vacuum induction furnace [17] and cast into ingots of 40 mm in diameter and 350 mm in length. After casting, the ingots were homogenised at 850°C for 24 h and then, in accordance with the diagram as shown in Fig. 1,

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subjected to various multi-variant thermomechanical and thermal processes including hot rolling, cold drawing, solution treatment and ageing. The ingots were hot rolled in the temperature range of 950→850°C into bars of 12 mm in diameter using a multiple stand shape rolling mill. Out of a part of the bars from the cold drawing process carried out with a chain drawbench at a deformation rate of 1.0 s^{-1}, semi-finished round products with diameter of 10.0 mm and 4.6 mm, which corresponds to deformation of approx. 30% and 85%, respectively, were made.

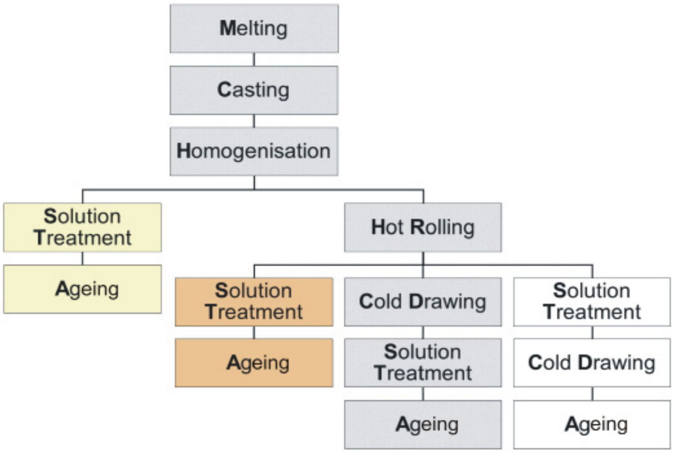

Fig. 1. Scheme of technological processes

For each of the implemented variants of thermomechanical and heat treatments (Fig. 1) the solution treatment and ageing were carried out under identical conditions. The solution treatment involved water cooling after prior holding at 900°C for 2 h. The ageing was carried out at 400, 450 and 500°C with air cooling for 1 to 48 hours.

After completion of each stage of the multi-variant processing (Fig. 1), the investigations of microstructure and hardness VHN/1 were carried out. Following selected process stages, phase composition, strength and plastic properties and electrical conductivity of the alloy were determined too.

Zwick hardness tester working at 9.8 N was used for hardness tests. The investigations of strength and plastic properties in static tensile test were carried out at room temperature with INSTRON 4469 testing machine.

The investigations of alloy microstructure were carried out with Nicon Epiphot 200 light microscope and Hitachi S-3400N scanning electron microscope. Preparation of materials for microstructure investigations involved the cutting with the use of spark erosion cutting-off machine, wet grinding, mechanical polishing on oxide and diamond pastes and etching in the mixture of 25 g ammonium persulphate and 100 ml water as well as the 15% nitric acid solution.

The observations of substructure were carried out with the use of scanning transmission electron microscope HITACHI HD-2300A. Preparation of thin foils involved pre-thinning and mechanical polishing to 15-20 mm thickness and electrolytic polishing in the solution containing 30% vol. nitric acid and 70% vol. methanol, at approx. 45°C and 10V.

The X-ray phase analysis was conducted with the use of Jeol JDX-7S diffractometer with a copper anode powered by 20mA at 40kV and a graphite monochromator.

The electrical conductivity was measured on cylindrical samples with a length-to-diameter ratio of 10:1. The measurement was taken at room temperature by conventional constant-current four-contact method [18].

3. Results and discussion

The Cu-3Ti ingots melted in a vacuum induction furnace and cast into a graphite mould show a characteristic dendritic microstructure with numerous precipitates of intermetallic phase, spheroid to elongated in shape, that are evenly arranged in the interdendritic spaces (Fig. 2). The X-ray analysis of phase composition of the alloy revealed that the two-phase microstructure consists of: the α phase, which is the titanium/copper solid solution, and the titanium-rich intermetallic Cu_3Ti phase (Fig. 3).

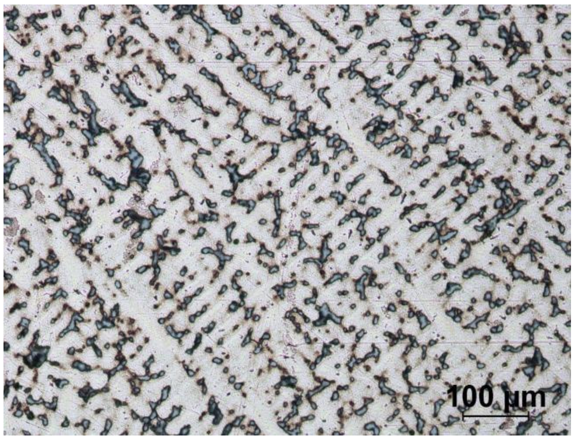

Fig. 2. Microstructure of cast Cu-3Ti alloy

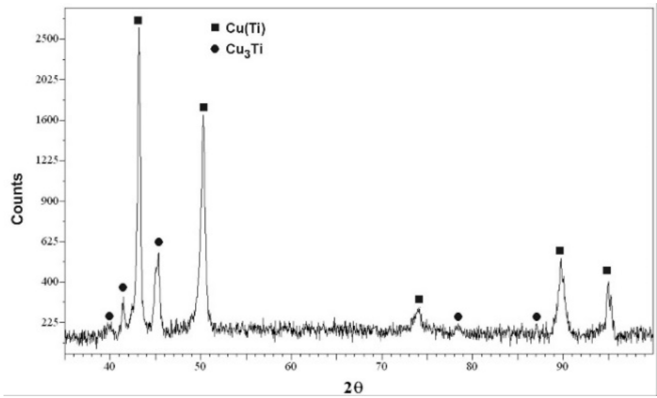

Fig. 3. XRD pattern of cast Cu-3Ti alloy

The dendritic microstructure, typical of post-casting alloys (Fig. 2), retains a similar nature after homogenising treatment (Fig. 4), although the relative volumes and sizes of intermetallic Cu_3Ti phase precipitates present in the interdendritic spaces are significantly smaller.

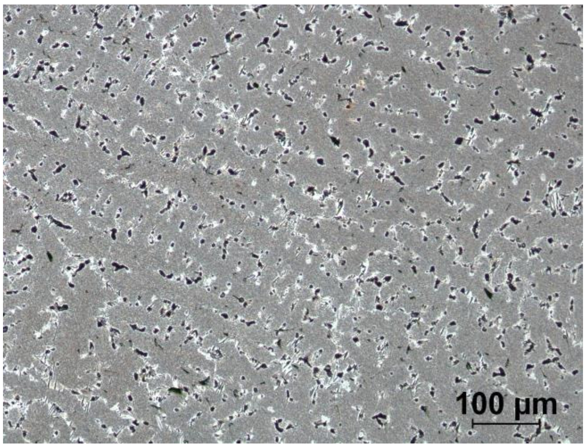

Fig. 4. Microstructure of homogenised Cu-3Ti alloy

The water solution treatment from 900°C of the alloy that was previously homogenised causes almost complete dissolution of the intermetallic Cu_3Ti phase precipitates (Figs. 4,5). This results in hardness decrease from 163 VHN, which is typical of an alloy after homogenising, to 103 VHN.

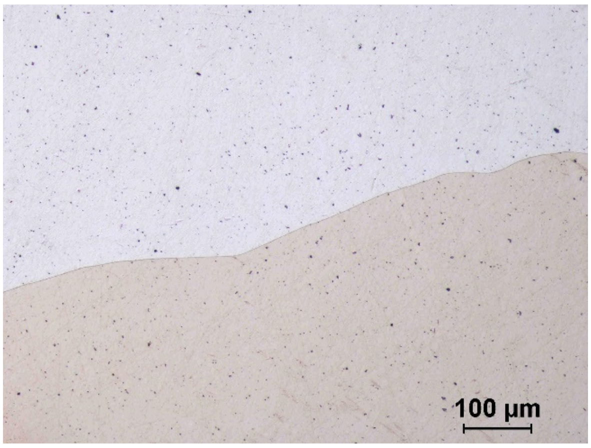

Fig. 5. Microstructure of Cu-3Ti alloy solution treated at 900°C for 2 h and quenched into water

The further ageing treatment conducted at 400, 450 and 500°C for up to 48 h indicates the possibility of hardening the Cu-3Ti alloy in the precipitation hardening processes (Fig. 6) due to the presence of secondary intermetallic phase precipitates with high dispersion in the microstructure of the aged alloy (Fig. 7). The ageing of the alloy at 400°C results in a continuous hardness increase over time, which is significantly higher in the initial period of ageing (up to 4 h). The alloy aged at this temperature achieves its highest hardness of 215 VHN after 48 h. Ageing at a higher temperature of 450 and 500°C enables to achieve of hardening on a much higher level. The highest hardness of 248 VHN was demonstrated by the alloy aged at 450°C for 24 h (Fig. 6). After ageing at 500°C, the maximum hardness level is lower and amounts to 225 VHN, although it is achieved over a much shorter time (4 h). In the alloy aged at 400°C for up to 48 h, the so-called overageing effect, which manifests itself in a decrease in hardness, does not occur (Fig. 6). This effect occurs in the alloy aged at 450 and 500°C after 24 and 4 h, respectively. At 500°C, the decrease in hardness is large enough that the hardness of alloy after 24 h of ageing is lower than the hardness of alloy aged at 400°C for the same time. The indication of overageing is, among other things, the characteristic effects of discontinuous precipitation at the grain boundaries of the aged alloy, particularly visible after long times of ageing (Fig. 8).

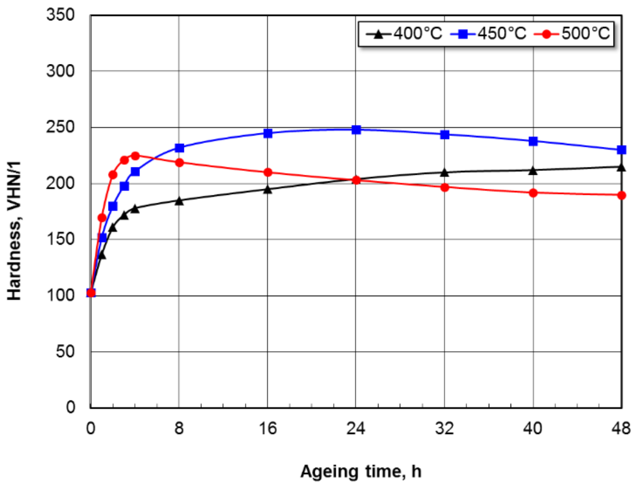

Fig. 6. Age hardening of cast Cu-3Ti alloy

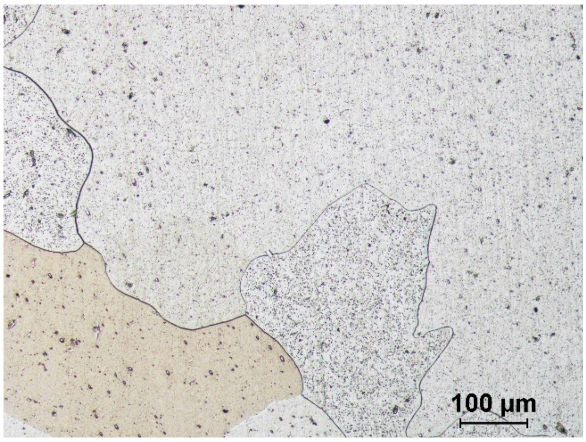

Fig. 7. Microstructure of cast Cu-3Ti alloy peak aged at 450°C for 24 h

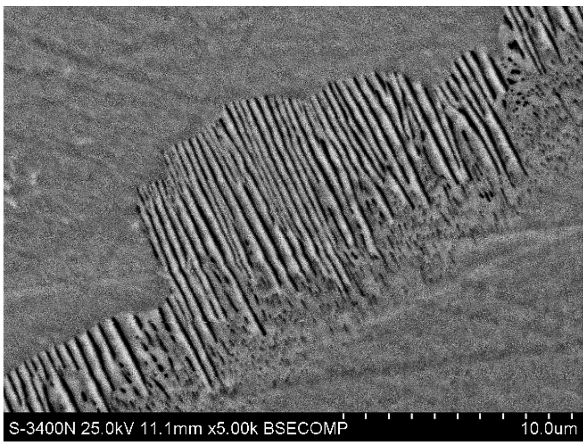

Fig. 8. Microstructure of cast Cu-3Ti alloy overaged at 450°C for 48 h

After hot rolling, the investigated Cu-3Ti alloy is characterised by a uniform, equiaxial grain microstructure of moderate grain size with large precipitates of the intermetallic Cu_3Ti phase at the grain boundaries and considerably smaller ones inside (Fig. 9).

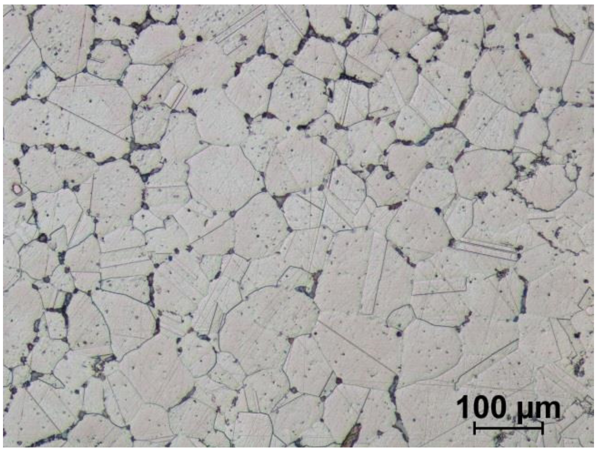

Fig. 9. Microstructure of hot rolled Cu-3Ti alloy

The hardness of Cu-3Ti alloy after hot rolling, cold drawing with total deformation of 85% and water solution treatment from 900°C is 145 VHN. Although it enabled to obtain the hardness of 229 VHN after 48 h, the ageing of this alloy at 400°C has not resulted in obtaining the maximum level of hardening (Fig. 10). This effect was achieved after ageing at a higher temperature of 450 and 500°C (at the level of 280 and 268 VHN, respectively) after 16 and 4 h of ageing. The alloy overageing at 450 and 500°C results in a decrease in hardness, which is particularly high after ageing at 500°C (Fig. 10). The hardness of the alloy aged at 500°C after 32 h of ageing is close to, and after having exceeded 40 h lower than, the hardness of the alloy aged at 400°C for the same time.

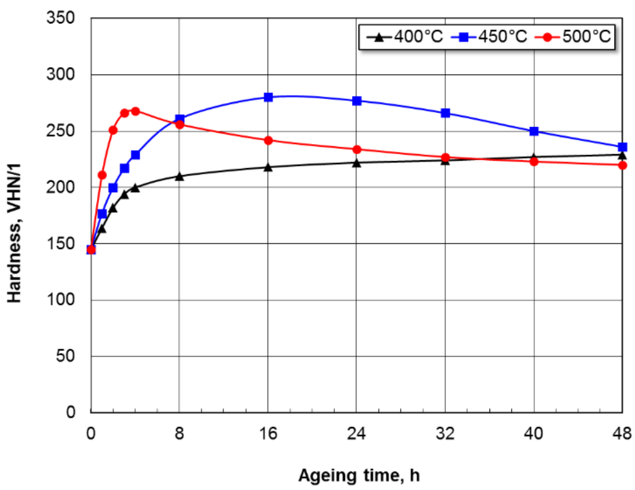

Fig. 10. Age hardening of hot rolled and cold drawn (85%) Cu-3Ti alloy

The effect of deformation applied during the cold drawing process preceding the solution treatment on hardness of the Cu-3Ti alloy aged at 450°C is shown in (Fig. 11). The increase in the value of cold deformation from 0 to 85% resulted in the higher maximum hardness (221 VHN for non-deformed alloy, 260 VHN for alloy after 30% deformation and 280 VHN for alloy after 85% deformation) achieved after ageing in increasingly shorter time of 32, 24 and 16 h.

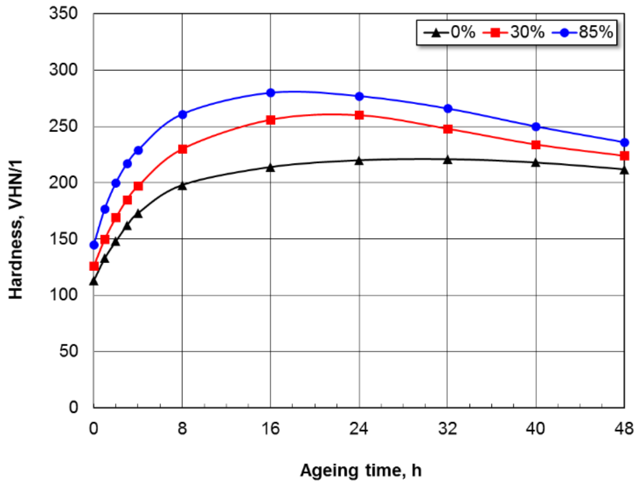

Fig. 11. Effect of cold drawing on hardness of Cu-3Ti alloy hot rolled, cold drawn, solution treated and aged at 450°C

In the microstructure of the Cu-3Ti alloy that was hot rolled, cold deformed with 85% reduction and solutioned in water from 900°C, the precipitates of the intermetallic Cu_3Ti phase undissolved under the solution treatment conditions that occur at the uniaxial grain boundaries are visible only (Fig. 12a). Short term ageing as well as ageing in time after which the alloy reaches its maximum hardening does not result in significant changes in its microstructure (Fig. 12b,c). Major microstructural changes in the form of characteristic lamellar precipitates occurring at the grain boundaries as a result of discontinuous precipitation are visible only after the alloy that has been overaged (Fig. 12d).

The use of low-temperature thermomechanical treatment during which the cold deformation was applied between the solution treatment and ageing allows a higher level of hardening to be obtained for the investigated Cu-3Ti alloy. The hardness of the Cu-3Ti alloy after hot rolling, solution treatment in water from 900°C and cold drawing with a total deformation of 85% reaches the level of 276 VHN, which is close to the value of 279 VHN obtained after the application of precipitation hardening following hot and cold plastic deformation (Fig. 10). The application of additional ageing results in further increasing in hardness up to 300, 340 and 332 VHN after ageing at 400, 450 and 500°C, respectively (Fig. 13). While the maximum hardness for ageing at 400°C is achieved only after 32 h of ageing, then in case of ageing at 450 and 500°C the maximum hardness is achieved as early as after 2 and 3 h of ageing, respectively. In this variant of the treatment, the alloy overageing at 400°C resulting in a decrease in hardness is minimal (Fig. 13). It is much more visible after ageing at 450 and 500°C (Fig. 13). It is so high that the hardness of the alloy aged at 450°C is after

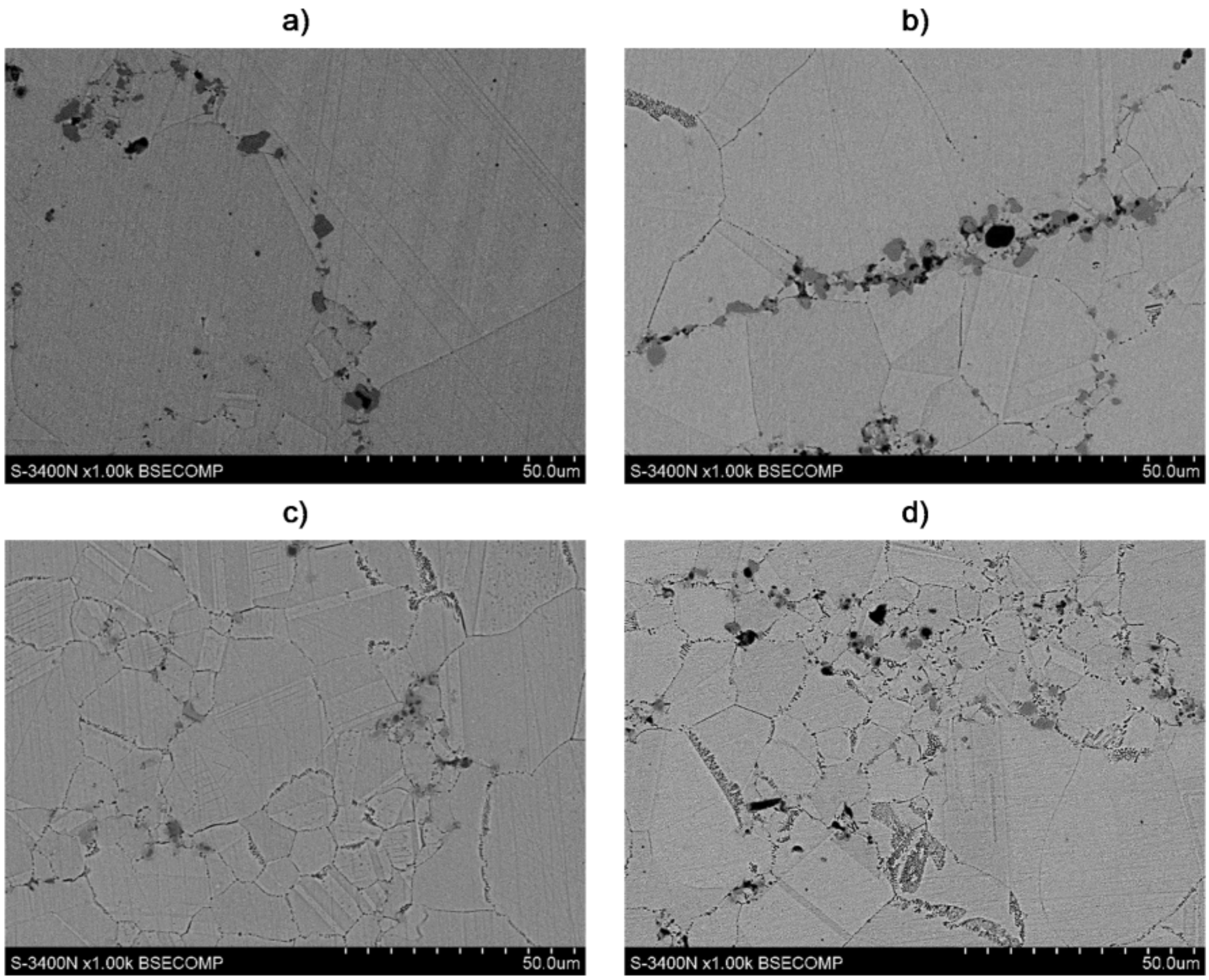

Fig. 12. Microstructure of Cu-3Ti alloy hot rolled, cold drawn (85%), solution treated (a) and aged at 450°C for 1 h (b), 4 h (c), 48 h (d)

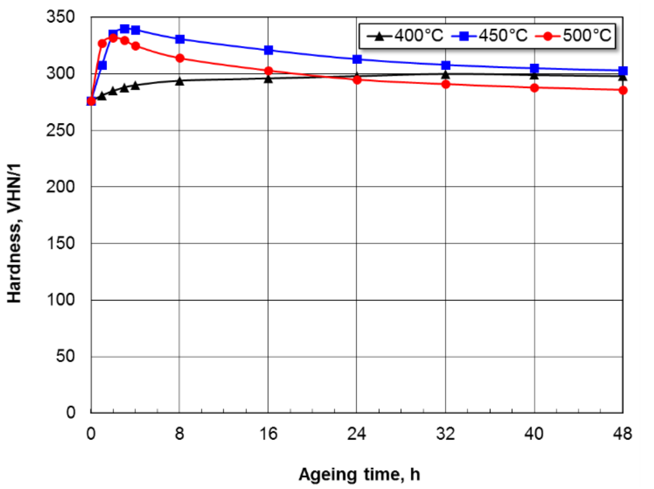

Fig. 13. Age hardening of hot rolled, solution treated and cold drawn (85%) Cu-3Ti alloy

48 h of ageing close to the maximum hardness of the alloy aged at 400°C. Similarly, the hardness of the alloy aged at 500°C is already after 24 h of ageing lower than the hardness of the alloy aged at 400°C for the same time.

The effect of deformation applied during the cold drawing process preceding the ageing on hardness of the Cu-3Ti alloy aged at 450°C is shown in (Fig. 14). The increase in the value of cold deformation from 0 to 85% resulted in the higher initial hardness before ageing and maximum hardness (221 VHN for non-deformed alloy, 267 VHN for alloy after 30% deformation and 340 VHN for alloy after 85% deformation) achieved after ageing in increasingly shorter time of 32, 8 and 3 h.

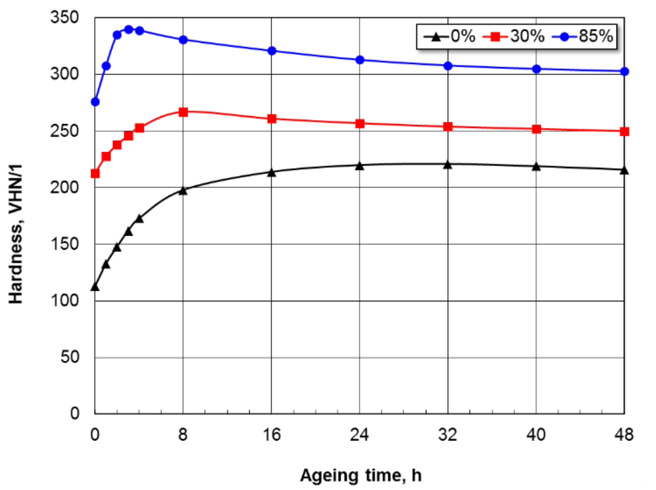

Fig. 14. Effect of prior cold drawing on hardness of Cu-3Ti alloy hot rolled, solution treated, cold drawn and aged at 450°C

In the microstructure of the Cu-3Ti alloy that was hot rolled, solutioned in water from 900°C and cold deformed with 85% reduction, large precipitates of the intermetallic Cu_3Ti phase undissolved during the solution treatment that occur at the grain boundaries are visible only (Fig. 15a). With increase in the time of ageing the relative volume of the hardening phase precipitates is increasing in the microstructure of the alloy, rather evenly within the space of the whole grain (Fig. 15b-d). In the microstructure of the overaged alloy, even after long time of ageing (Fig. 15d), no characteristic effects of discontinuous precipitation, which are visible in the microstructure of the overaged alloy after casting (Fig. 8) and after hot rolling and cold drawing (Fig. 12d), were observed. In this case, the only noticeable indications of alloy overageing are the reduction in dispersion of the hardening phase precipitates and increase in their size (Fig. 15).

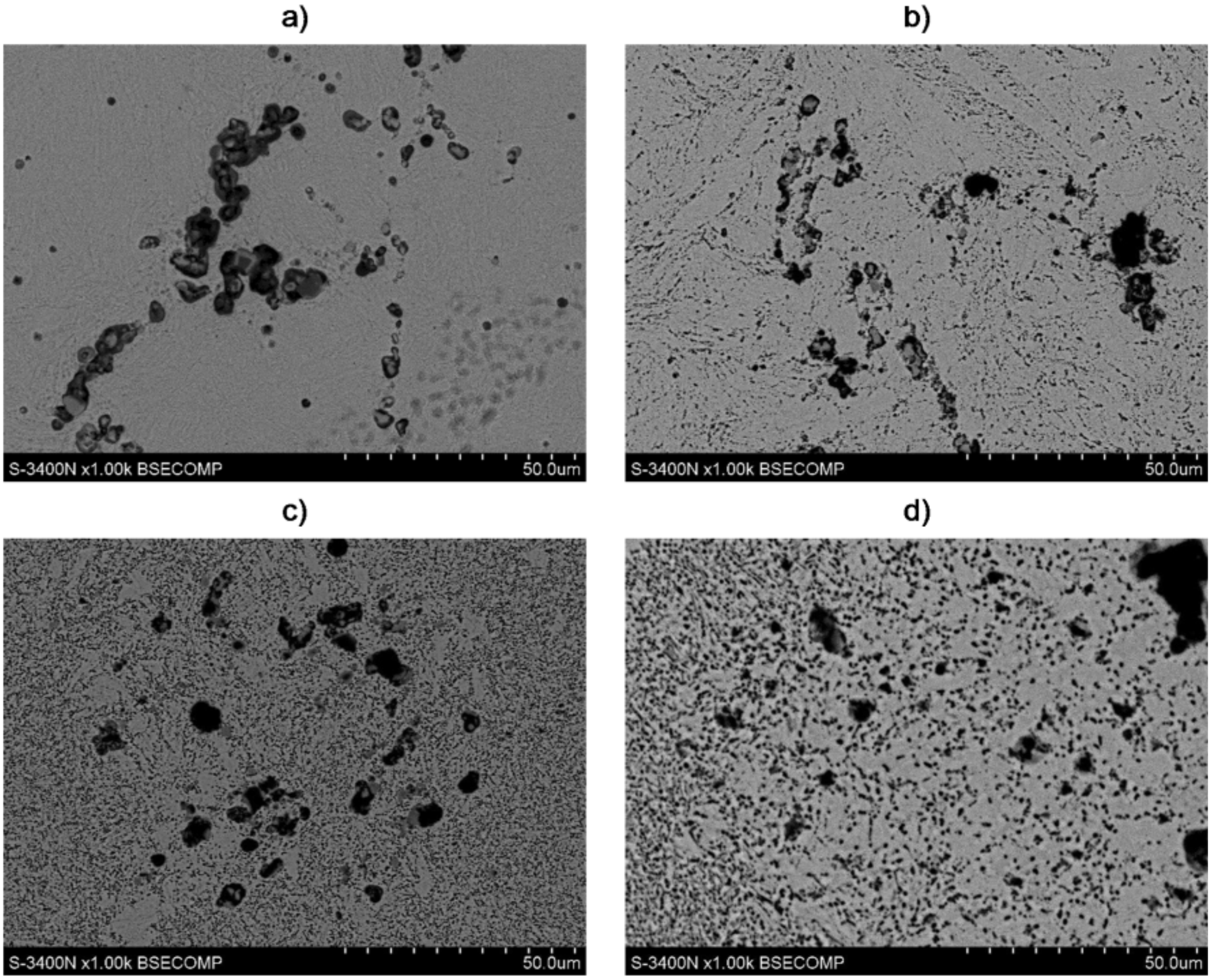

Fig. 15. SEM microstructure of Cu-3Ti alloy hot rolled, solution treated, cold drawn (85%) (a) and aged at 450°C for 1 h (b), 3 h (c), 48 h (d)

Transmission electron microscopy investigations of the Cu-3Ti alloy that was hot rolled, solutioned in water from 900°C, cold deformed with 85% reduction and aged at 450°C to provide maximum hardening revealed presence in its microstructure of the hardening Cu_4Ti phases, partially coherent with the matrix, after a shorter time of ageing (Fig. 16a) as well as the equilibrium Cu_3Ti phase after ageing in sufficient time to obtain maximum hardening (Fig. 16b).

The Cu-Ti alloys, which are to be cheaper and non-toxic substitutes for beryllium bronzes, are expected to show equally high strength properties while maintaining the maximum electrical conductivity, min. 17% IACS [4,5] – 17% of pure copper's conductivity. The final mechanical properties and electrical conductivity of the Cu-Ti alloys are determined by selection of titanium contents, mechanical working conditions and hardening heat treatment including solution treatment and ageing. Thus, for an Cu-3Ti alloy, the selection of parameters for thermomechanical and thermal processes is decisive for shaping its final mechanical properties and electrical conductivity.

Table 1 summarises mechanical properties and electrical conductivity of the investigated Cu-3Ti alloy both in the as-cast condition and after various thermal and thermomechanical hot and cold processes. Mechanical properties and electrical conductivity of the cast Cu-3Ti alloy after homogenising are far from those expected. Solution treatment and ageing of the alloy under conditions that make it possible to obtain maximum hardness results in insufficient improvement in mechanical properties and electrical conductivity. After hot rolling, cold drawing with total

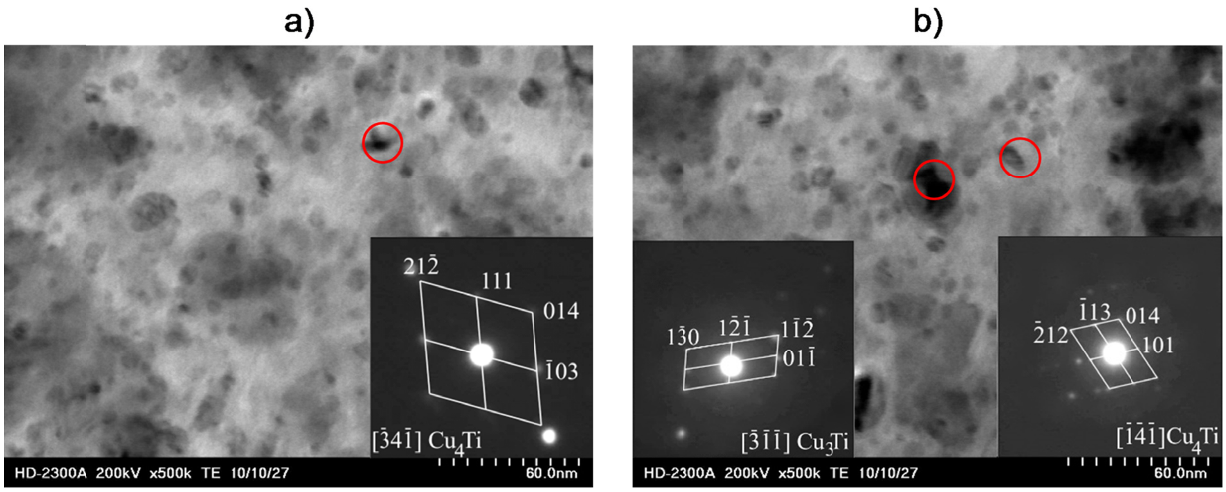

Fig. 16. Transmission electron micrographs (bright field and diffraction) of Cu-3Ti alloy hot rolled, solution treated, cold drawn (85%) and aged at 450°C for 1 h (a), 3 h (b)

deformation of 85% as well as solution treatment and ageing under conditions enabling to get maximum hardness, the minimum required electrical conductivity (17% IACS) at tensile strength of 850 MPa and satisfactory plasticity (EL = 21.0%) was obtained. Overageing of the alloy under such conditions results in a slight change in its mechanical properties and electrical conductivity only (Table 1). The use of low-temperature thermomechanical treatment after hot rolling allows the minimum required electrical conductivity to be obtained as early as after slight overageing of the alloy under conditions ensuring maximum hardening at a much higher tensile strength of 1095 MPa and much lower plasticity (EL = 8.5%). Complete overageing of the alloy under such conditions results in reduction in its tensile strength to 700 MPa, moderate increase in plasticity from 8.5 to 12.6% and very high increase in electrical conductivity up to 30.5% IACS, which is close to that of beryllium bronzes (Table 1).

Mechanical properties and electrical conductivity of the Cu-3Ti alloy in various thermal and thermomechanical conditions were compared to properties of an alloy with comparable Ti content, described in [19], and the Cu-2.0Be-0.5Co alloy that the alloy under investigation may be a substitute for, described in [16]. Data in Table 2 show that the investigated Cu-3Ti alloy

TABLE 1

Mechanical properties and electrical conductivity of Cu-3Ti alloy in various thermal and thermomechanical conditions

No.	Thermal and thermomechanical conditions	Hardness, VHN/1	Tensile strength, MPa	Elongation, %	% IACS
1	Homogenisation	163	425	22.0	10.5
2	Solution treatment	103	390	26.5	5.5
3	Solution treatment + ageing: 450°C/24 h	248	525	19.5	11.0
4	Hot rolling + cold drawing (85%) + solution treatment	145	520	36.5	4.0
5	Hot rolling + cold drawing (85%) + solution treatment + ageing: 450°C/16 h	280	850	21.0	17.0
6	Hot rolling + cold drawing (85%) + solution treatment + ageing: 450°C/48 h	236	845	21.5	18.0
7	Hot rolling + solution treatment + cold drawing (85%)	276	1040	5.8	4.0
8	Hot rolling + solution treatment + cold drawing (85%) + ageing: 450°C/3 h	340	1150	7.5	15.5
9	Hot rolling + solution treatment + cold drawing (85%) + ageing: 450°C/4 h	340	1095	8.0	18.5
10	Hot rolling + solution treatment + cold drawing (85%) + ageing: 450°C/48 h	303	700	12.6	30.5

TABLE 2

Comparison of mechanical properties and electrical conductivity of investigated alloy with Cu-2.7 Ti [19] and Cu-0.5Be-2.5Co [16] alloys

No.	Property	Cu-3Ti			Cu-2.7Ti			Cu-0.5Be-2.5Co		
		ST	ST+A	ST+CD+A	ST	ST+A	ST+CD+A	ST	ST+A	ST+CD+A
1	Hardness VHN/1	145	279	340	120	275	355	90	215	225
2	Tensile strength, MPa	520	850	1150	430	680	1000	310	760	830
3	Elongation, %	36.5	21.0	7.5	36.0	22.0	3.5	25.0	15.0	8.0
4	% IACS	4.0	16.5	15.5	10.0	17.0	12.0	20.0	45.0	50.0

ST – Solution Treatment; A – Ageing; CD – Cold Drawing in comparable thermal and thermomechanical conditions exhibit higher strength and plastic properties in relation to the other two alloys and comparable electrical conductivity in relation to the Cu-2.7Ti alloy. Compared to the Cu-2.0Be-0.5Co alloy, the electrical conductivity of the investigated alloy is clearly lower. In the overaged condition, these differences decrease (Tables 1,2).

4. Conclusions

Mechanical properties and electrical conductivity of the cast Cu-3Ti alloy after both homogenising and additional solution treatment and ageing under conditions that make it possible to obtain maximum hardness are far from the expected ones, i.e. high strength, satisfactory plasticity and electrical conductivity of min. 17% IACS.

The completed investigations have shown that such properties can be obtained as a result of the use of hot working in combination with cold working, solution treatment and ageing or low-temperature thermomechanical treatment and ageing.

After hot rolling, cold drawing with total deformation of 85% as well as solution treatment in water from 900°C and ageing at 450°C for 16 h, the Cu-3Ti alloy is characterised by the required electrical conductivity (17% IACS) at tensile strength of 850 MPa and elongation of 21.0%. Complete overageing of the alloy results in a slight change in its mechanical properties and electrical conductivity only.

The Cu-3Ti alloy obtains the same level of electrical conductivity, but at a much higher tensile strength of 1095 MPa and lower elongation of 8.5%, after hot rolling and low-temperature thermomechanical treatment ended with ageing at 450°C for 4 h. Complete overageing of the alloy results in reduction in its tensile strength to 700 MPa, slight increase in elongation up to 12.6% and very high increase in electrical conductivity up to 30.5% IACS.

The beneficial properties of the Cu-3Ti alloy are the effect of grain refinement in hot rolling, strain hardening in cold drawing and precipitation hardening due to presence of dispersing, partially coherent precipitates of metastable Cu_4Ti phase and stable Cu_3Ti phase.

An important parameter that determines the level and course of the Cu-3Ti alloy hardening processes is the value of total deformation applied in cold drawing. The higher deformation value the higher level of hardening after ageing and shorter time required to obtain it.

The investigated Cu-3Ti alloy shows higher strength and plastic properties and comparable thermal conductivity in relation to those of the Cu-2.7Ti alloy with similar titanium content which is described in the literature [19]. Compared to the Cu-2.0Be-0.5Co beryllium bronze that the Cu-3Ti alloy under investigation could be a substitute, its mechanical properties are significantly higher, while the electrical conductivity is significantly lower.

The investigations have shown that the Cu-3Ti alloy and the semi-finished products made out of it, especially with the involvement of low-temperature thermomechanical treatment, are characterised by properties that give reasons to think about them as substitutes for very expensive and toxic beryllium bronzes in the applications that require high mechanical properties and moderate electrical conductivity, and after overageing also in the applications that require high electrical conductivity.

Acknowledgment

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