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MICROSTRUCTURE AND SERVICE PROPERTIES OF COPPER ALLOYS

This elaboration shows the effect of combined heat treatment and cold working on the structure and utility properties of alloyed copper. As the test material, alloyed copper CuTi4 was employed. The samples were subjected to treatment according to the following schema: 1st variant – supersaturation and ageing, 2nd variant – supersaturation, cold rolling and ageing. The paper presents the results of microstructure, hardness, and abrasion resistance. The analysis of the wipe profile geometry was realized using a Zeiss LSM 5 Exciter confocal microscope. Cold working of the supersaturated solid solution affects significantly its hardness but the cold plastic deformation causes deterioration of the wear resistance of the finally aged CuTi4 alloy.

Keywords: alloyed copper, heat treatment, cold rolling, wear resistance, hardness

1. Introduction

Literature data [1-5] make it possible to state that the method most frequently used to improve the mechanical properties of CuTi alloys is ageing, during which phases precipitate, deciding their service properties. This process is usually realised at temperatures of 400–700°C for 1 to 48 hours. It has been found that strengthening of the alloys occurs if the plastic working employed includes cold rolling before ageing [6–16].

Increase of the mechanical properties and electrical conductivity can be controlled by changing the recrystallization and precipitation kinetics. Therefore, there are used different variants of treatment consisting the combined sequence of heat treatment and cold rolling [12, 13].

Addition of titanium alone at concentrations up to 4.29% increases the hardness, the strengthening of the solution increases the fatigue strength. This is due to the large difference in atomic radii of copper and titanium (r_{Cu}=0,128 nm; r_{Ti}=0,145 nm), which results in considerable stress concentration in case of titanium atoms in the crystal lattice of copper. Further enhancing of Ti addition does not affect any further hardness increase [17].

It is essential to determine the effect of cold rolling after solution heat treatment on tribological resistance. This is related to the use of the CuTi alloys primarily in the energy industry and electronic industry (sealing electrodes), as well as for the production of equipment for mine rescue agencies and anti-terrorist units [18].

The aim of this study was to determine the relation how deformation strengthening and aging parameters affect the resistance of the CuTi4 alloy as well as on the microstructure and functional properties.

2. Material and methods

The starting material was an ingot made of CuTi4 alloy hot-rolled to a thickness of 3.0 mm. The chemical composition is given in Table 1.

Hot-rolled strips, after cleaning of their surface (etching, rinsing, drying) were cut into samples (with dimensions of 3×25×30 mm) and were assigned for further investigations. The samples were subjected to further treatment according to the following schema:

1st variant

Samples were held at a temperature of 900°C for 1 hour in an electric resistance chamber furnace. The heated samples were intensively water-cooled after taking them out of the furnace chamber. The time from taking the sample from the furnace to immersing it in water did not exceed 2 seconds. After cooling down, some samples were assigned for testing of their properties after supersaturation, and the remaining ones were aged at temperatures of 450, 500, 550, and 600°C for 1, 5, 15, 30, 60, 120, and 420 minutes. The material prepared in this way was the subject of subsequent investigations.

TABLE 1

Chemical composition of CuTi4 alloy

Cu	Ti	Zn	P	Pb	Sn	Mn	Ni	Sb	Bi	As	Cd
95.830	3.950	0.130	0.065	0.003	0.009	0.030	0.010	0.001	0.001	0.001	0.001

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2nd variant

Supersaturated samples were cold-rolled after water cooling using the 50% draft (3.0 →1.5 mm).The ageing process was carried out using the same parameters as in the 1st variant.

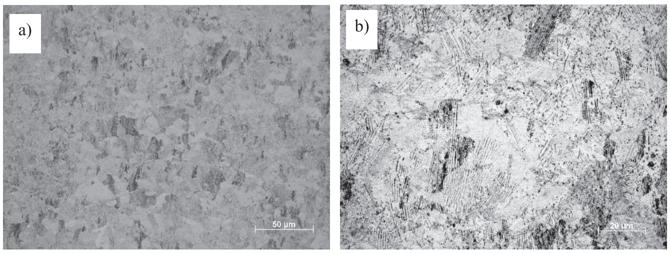
Wear resistance tests were carried out on a Taylor Hobson tribometer. A counter-specimen in the form of a ball with 6 mm diameter was made from Al_2O_3 and the load was 10 N. Each measurement consisted of 5000 cycles each of 7.2 mm. The total distance covered by the sample each time was 36 m.

The wear profile geometry was examined using the Zeiss LSM 5 Exciter confocal microscope with an observation system using 4 lasers with visible wavelengths from 405 to 633 nm, and with the ZEN and Axio Vision image acquisition and analysis system.

The path of the wear groove were examined on a Zeiss Supra 25 scanning electron microscope (SEM).

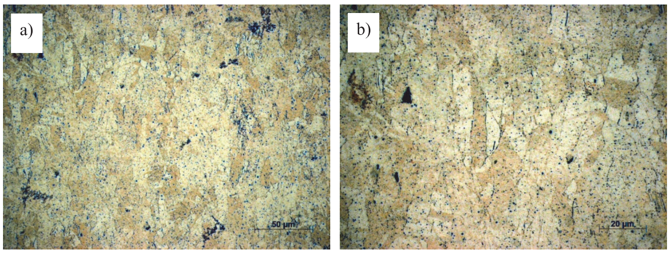
3. Results and discussion

After supersaturation and subsequent ageing at a temperature of 450°C for 60 minutes, grains are visible in the microstructure, whose average diameter is ca. 100 µm, as well as others whose average diameter is 20–50 µm. Therefore, this structure is not homogeneous. Annealing twins are also visible in the microstructure, being most probably the result of supersaturation. After supersaturation and subsequent ageing at a temperature of 600°C for 60 minutes, no grains were found in the microstructure whose average diameter exceeded 50 µm (Fig. 1a). The dominant grains have an average diameter within the range of 20–50 µm, with a shape close to spherical. No annealing twins were revealed, but lamellar precipitations are visible in the grains (Fig. 1b).



In the microstructure of the supersaturated and cold-rolled (50% draft) alloy, the occurrence of multiple deformation bands was found, in which the average grain diameter is several hundred percent smaller than that of those outside the bands. This is the effect of the uneven dissolving of titanium in the matrix, which resulted in a varying concentration of Ti in the neighbouring grains [20].

The CuTi4 alloy after supersaturation, cold-rolling and ageing at 450°C for 60 minutes is characterised by a microstructure in which the dominant grains have an elongated shape in the form of bands (lamellae) with a width of 10–20 µm and length of 20–30 µm. In the microstructure of the CuTi4 alloy that was supersaturated, cold-rolled and aged at 600°C for 60 minutes, grains were revealed with an elongated shape with a width of 5–10 µm and length of 20–30 µm (Fig. 2).



Changes occurring in the microstructure which are the effect of the spinodal decomposition, continuous and discontinuous precipitations cause changes in the investigated alloy properties. Based on the hardness tests results it is possible to infer that the employment of cold working between supersaturation and ageing (variant 2) causes an increase in hardness (Table 2). The hardness increased by 76% and is 220 HV compared to the supersaturated state (125 HV). The cold-worked alloy, then aged at the temperatures of 400 and 500°C, acquired a hardness 30% higher than the not deformed alloy processed with the same parameters. The supersaturated alloy, cold-rolled and aged at 450°C, does not change its hardness virtually within the entire investigated time period, whereas, after ageing at the temperatures of 550 and 600°C its hardness increases to the ageing time of t=60 min, and then, with further ageing time, a rapid increase in hardness occurs.

Ageing of CuTi4 alloy for more than 120 minutes at 450°C results in a reduction of hardness. For the not deformed alloy, continuous increase of hardness was observed in the investigated range. On the other hand, for the rolled alloy, ageing at a temperature of 500°C for more than 30 min causes the hardness to decrease, whereas for the not deformed alloy this occurs only after 120 minutes. Next, with increase of the ageing temperature, a reduction of the hardness of the deformed alloy occurs also after 30 minutes, but quite radically, from the value of 265 HV to ca. 150 HV (Table 2)

The increase in hardness after treatment according to variant 2, compared to the classic heat treatment (variant 1), is caused by the strain hardening. This is clearly visible for each of the investigated ageing temperatures at the initial range of the treatment period (1, 10 minutes), The recovery and recrystallization process, demonstrated by the significant drop in hardness, occurs rapidly with extension of the ageing time, and especially at the temperatures of 550 and 600°C.

After five years of the samples preparation the hardness testing was repeated. All the time the sample were stored at surrounding temperature and atmospheric pressure. It was found that the CuTi4 alloy treated according to the I variant is characterised by a higher hardness than five years ago (Fig. 3), while the alloy treated according to the second variant is characterized by an unexpected decrease in hardness (Table 2, Fig. 3) compared to the values obtained before. The obtained results require confirmation using other research techniques.

Based on the hardness changes, depending on the treatment type and parameters, one might expect that cold working will increase the abrasion wear resistance. However, the investigation results reveal quite the opposite relationship.

TABLE 2

Hardness measurements results of the CuTi4 alloy for both treatment variants

Aging temperature, T [°C]	Aging time, t [min]	Hardness, HV5	
		Z=0%	Z=50%
450	1	137	221
450	15	202,3	292
450	30	223	297
450	60	229	296
450	120	236	298
450	420	248	283
500	1	147	225
500	15	219	300
500	30	226	287
500	60	236	279
500	120	244	263
500	420	183	240
550	1	132	265
550	15	228	273
550	30	235	245
550	60	218	218
550	120	189	160
550	420	178	157
600	1	135	256
600	15	259	251
600	30	187	167
600	60	177	162
600	120	178	158
600	420	170	152

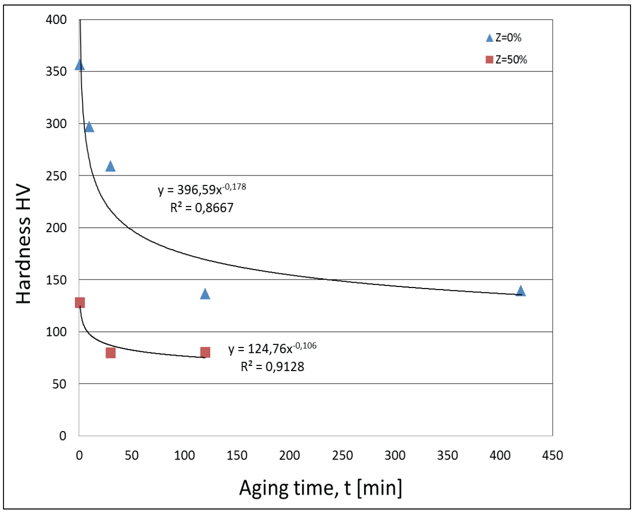


Fig. 3. Hardness changes of CuTi4 alloy supersaturated at temperature 900°C/1h/water and aging at 550°C versus ageing time

It was found, based on tribological tests results, that the supersaturated alloy, rolled and aged (variant 1) is characterised by a reduced abrasion wear resistance compared to the alloy treated according to variant 2. This is because the recrystallization and precipitation kinetics are different from those in the alloy subjected to the precipitation hardening. The CuTi4 copper alloy subjected to soaking for 60 minutes and then supersaturated from a temperature of 900°C in water is characterised by a wear trace of 324.5 mm^2. The supersaturated alloy that is aged next is characterised by higher abrasion wear resistance than the supersaturated alloy that is cold-rolled and then aged (Figs. 4–6). The wear of the cold not deformed alloy grows with extension of the ageing time.

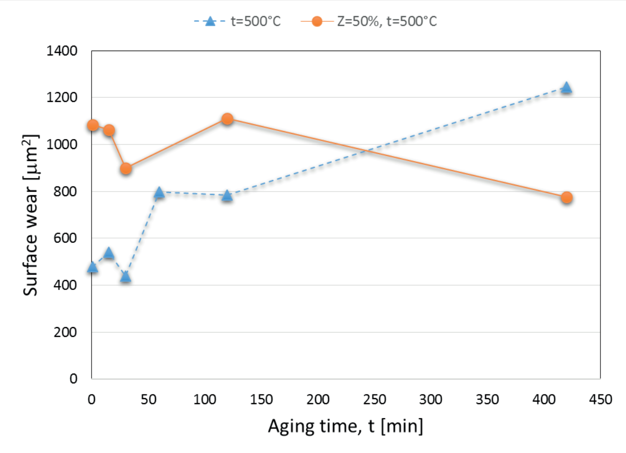


Fig. 4. Influence of ageing time at temperature of 500°C and cold rolling on abrasion wear of CuTi4 alloy supersaturated from temperature of 900°C

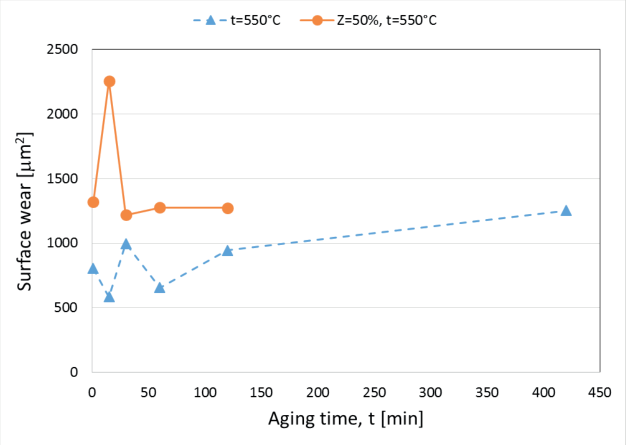


Fig. 5. Influence of ageing time at temperature of 550°C and cold rolling on abrasion wear of CuTi4 alloy supersaturated from temperature of 900°C

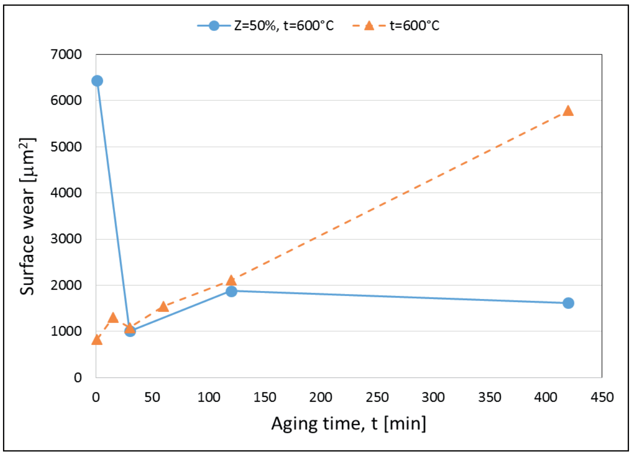


Fig. 6. Influence of ageing time at temperature of 600°C and cold rolling on abrasion wear of CuTi4 alloy supersaturated from temperature of 900°C

TABLE 3

Results of tribological tests of CuTi4 alloy; wear trace [mm^2]

Ageing time [min]	Ageing temperature [°C]						
	450°C	500°C		550°C		600°C	
	Z=0	Z=0	Z=50%	Z=0	Z=50%	Z=0	Z=50%
1	–	479	1085	803	1319	828	6433
15	334	541	1063	584	2255	1299	–
30	560	439	899	–	1218	1084	1010
60	–	796	–	656	1276	1543	–
120	694	785	1111	944	1273	2109	1880
420	976	1246	777	1251	–	5783	1620

The abrasion wear resistance test results are presented in Table 3.

Figures 7–9 present a comparison of the tribological wear resistance of the CuTi4 alloy supersaturated and aged (variant 1), and of the supersaturated alloy, cold-worked and aged (variant 2) for 5 (Fig. 7), 15 (Fig. 8), and 120 minutes (Fig. 9). With increasing ageing time, the tribological resistance of the alloy processed according to variant 2 demonstrates a declining tendency, whereas the abrasion wear of the alloy processed according to variant 1 grows with extension of its ageing time. The increased abrasion wear in variant 2 of the treatment is a consequence of the occurrence of strain-free zones. In these locations the alloy is especially susceptible to abrasion wear, as it is locally softer than the deformed matrix. On the other hand, the growing abrasion wear of the not deformed alloys is explained by the growth of the precipitations (phases) which reinforce the alloy. With the growth of these precipitations, the matrix is deprived successively of the dissolved component. As the initially small precipitations grow, their dimensions increase, but they automatically decrease in number (because of absorption and addition of some precipitations by others) and the distance among the precipitated particles grows. With a sufficiently long ageing time, the growing particles of the second phase lose coherence with the matrix. This results in a reduction of the abrasion wear resistance with extension of the ageing time.

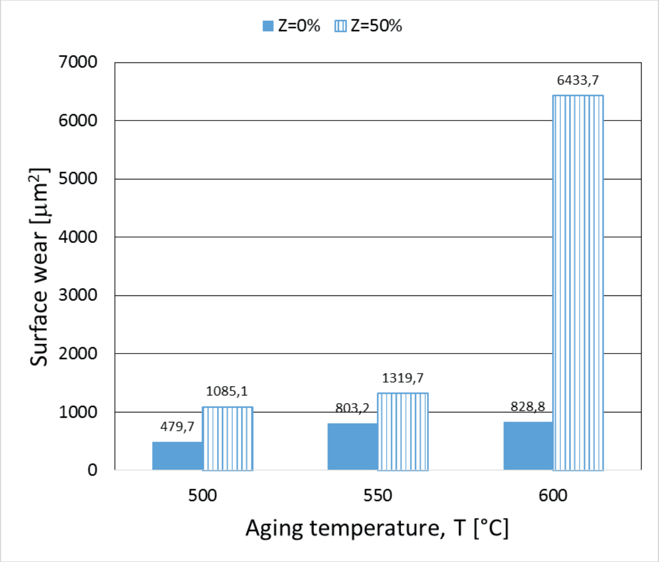


Fig. 7. Comparison of tribological wear resistance of CuTi4 alloy supersaturated and aged for 5 min, and supersaturated, cold worked and aged for 5 minutes

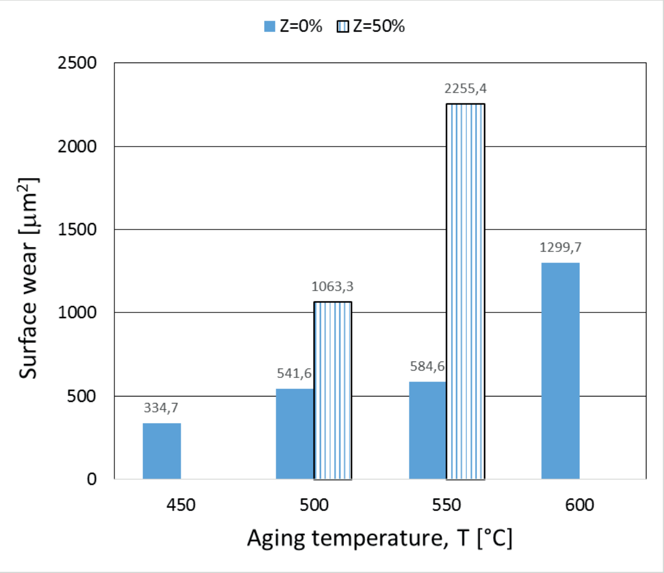


Fig. 8. Comparison of tribological wear resistance of CuTi4 alloy supersaturated and aged for 15 min, and supersaturated, cold worked and aged for 15 minutes

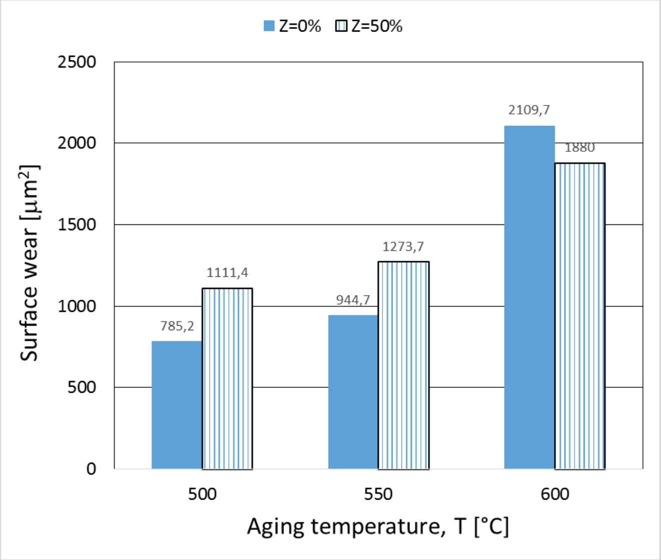


Fig. 9. Comparison of tribological wear resistance of CuTi4 alloy supersaturated and aged for 120 minutes, and supersaturated, cold worked and aged for 120 minutes

The effect of the treatment according to variant 2 is visualised by the scratch groove coastline shape (Fig. 10) and is also visible on the transverse section of the scratch groove (Fig. 11). Based on the scratch groove shape (being the effect of the abrasion wear resistance measurement), one can state that cold working causes a reduction of the abrasion wear resistance (Fig. 12). For both ageing times, the deformed alloy after supersaturation demonstrates a lower abrasion wear resistance. The larger standard deviation value attests also to the lower structural homogeneity than in case of the not deformed alloy. Ageing for a very short time (5 minutes) causes the abrasion wear resistance to increase (Table 4). However, this resistance becomes less as the ageing time is extended. This is connected with precipitation, in the initial ageing period, of the metastable particles of the β'-Cu_4Ti phase coherent with the matrix, which are responsible for the alloy strengthening effect. However, in the succeeding ageing phase, the β'-Cu_4Ti particles dissolve and the stable, equilibrium β-Cu_3Ti, phase precipitates, which loses its coherence with the matrix as the ageing time is extended. It is this loss of coherence that causes the abrasion wear resistance of the CuTi4 alloy to drop.

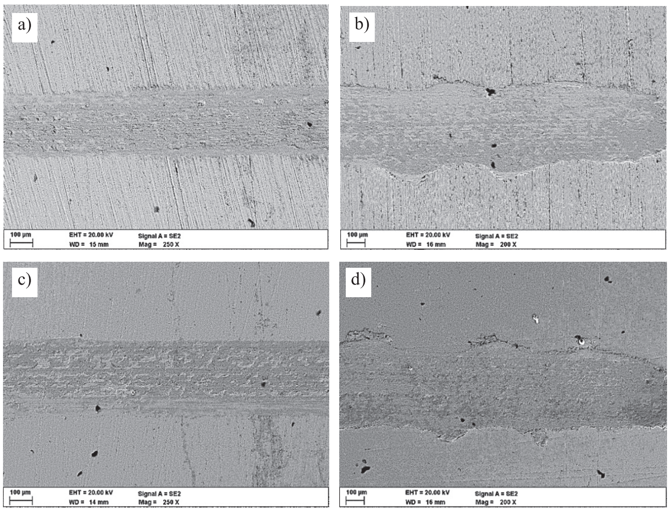


Fig. 10. Scratch groove made with indenter from Al_2O_3 on CuTi4 alloy surface, supersaturated and aged at temperature of 500°C for a) 5 and c)120 minutes; supersaturated, cold worked, and aged at temperature of 500°C for b) 5 and d) 120 minutes

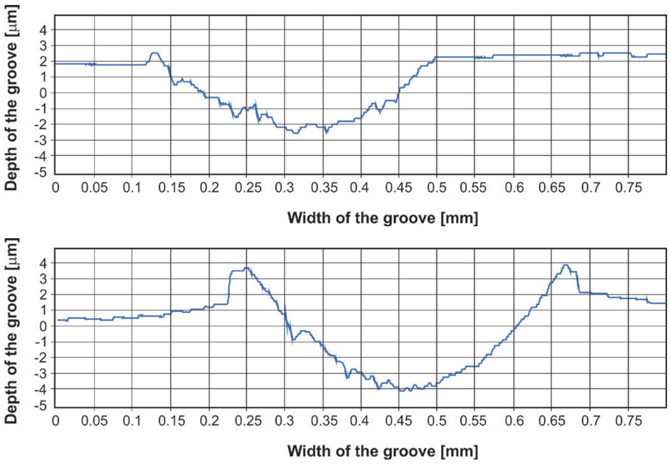


Fig. 11. Transverse scratch groove profile in CuTi4 alloy with indenter from Al_2O_3 , a) alloy supersaturated and aged at temperature of 500°C for 120 minutes, b) alloy supersaturated, cold worked (Z=50%) and aged at temperature of 500°C for 120 minutes

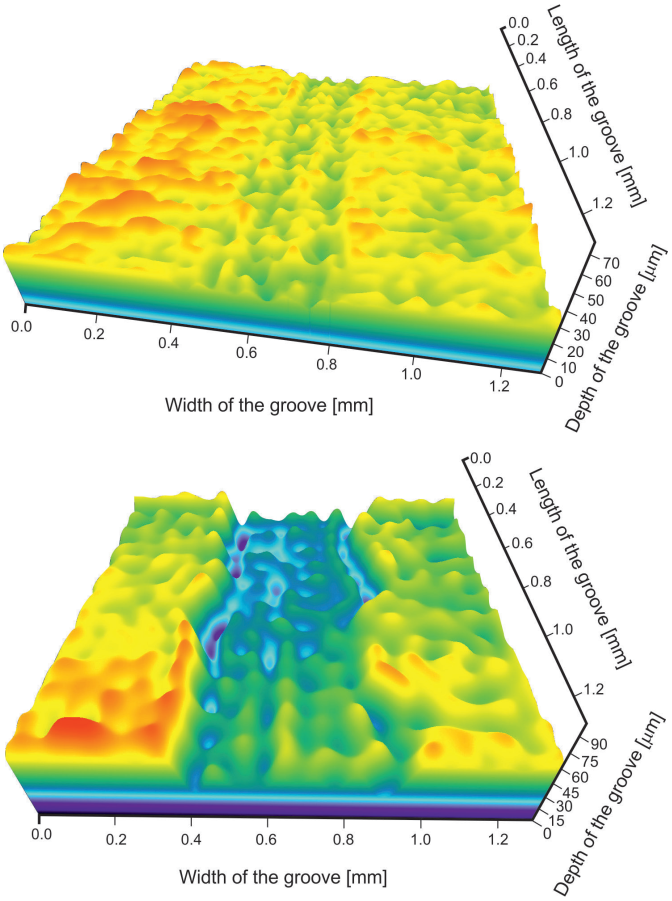


Fig. 12. Image of the scratch groove profile in CuTi4 alloy with indenter from Al_2O_3 a) alloy supersaturated and aged next at temperature of 500°C for 120 minutes, b)alloy supersaturated, cold worked (Z=50%), and next aged at temperature of 500°C for120 minutes, confocal microscope

As concerns the abrasion wear resistance, the heat treatment according to variant 1 (within a short time) causes its effective improvement also for the supersaturated state (Table 4).

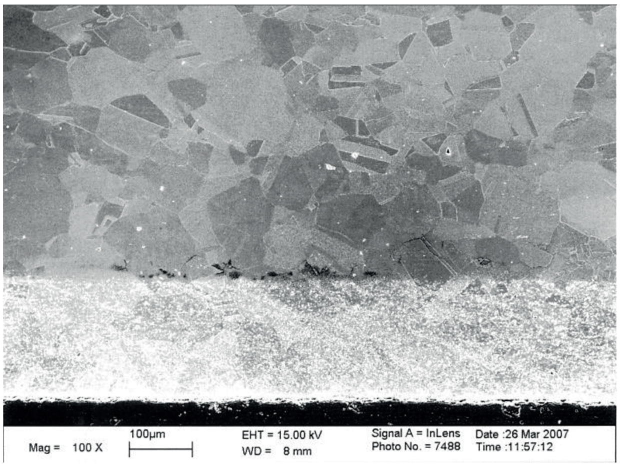


Fig. 13. Microstructure of the cross section of the CuFe2 alloy after ageing, with visible oxide layer [19]

TABLE 4
Width of scratch groove on surface of CuTi4 alloy after ageing at temperature of 500°C with indenter from Al_2O_3 calculated using SEM observations

Ageing time [min]	-	5		120	
draft	Z=0	Z=0%	Z=50%	Z=0	Z=50%
average value [mm]	400.0	287.9	469.6	335.5	444.0
Standard deviation	15.2	12.2	38.8	5.8	24.8

It was found when investigating the effects of the two treatment variants on the CuTi4 alloy's tribological wear resistance that variant 1 (supersaturation and ageing) ensures a higher abrasion wear resistance. Based on observation of the results obtained with SEM it was found not only that cold working after supersaturation causes higher abrasion wear, but that the width and coastline shape of the scratch groove made by the moving indenter are also different.

Greater abrasive wear of the alloy treated by variant 2 is related with the conditions of ageing, which - for economic reasons (the industrial environment) - were performed in air. Therefore the alloy subjected to cold rolling, with more particulate microstructure shows more intensive oxidation. The greater thickness of the oxidized surface layer caused lower resistance to abrasive wear. Similar results were obtained for the alloy CuFe2 in [19] (Fig. 13). Reduction of the wear resistance together with increasing of the deformation degree in the CuCr0.65 copper-chromium alloy has also been confirmed in work [20].

4. Conclusions

The most advantageous microstructure (for both treatment variants), determining stable properties of the alloy, is obtained after ageing at a temperature of 450°C for 120–240 minutes for the alloy without cold working and for 60–120 minutes for the rolled alloy. This is connected with the recrystallization process proceeding much more slowly compared to the precipitation process.

Structural analysis of the alloy made it possible to demonstrate the increase of structural refinement with extension of the ageing time of the cold-worked alloy after supersaturation. Cold working of the supersaturated solid solution has a significant effect on its hardness (Table 2). As concerns tribological wear resistance, employing the cold plastic deformation (variant 2) causes its deterioration (Figs. 4–6). It was found that the abrasion wear resistance of the CuTi4 alloy processed according to variant 2 is less than that of the alloy processed according to variant 1 (Figs. 7–9). However, the deformed alloys are characterised by better and more stable properties (e.g. hardness) for the investigated ageing time. As compared to the alloy processed according to variant 1, cold working of the supersaturated solid solution causes deterioration of the tribological wear resistance of the finally aged CuTi4 alloy. The wear trace of the alloy aged according to variant 2 is 134–205% greater than that of the alloy aged according to variant 1.

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