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PRECIPITATION STRENGTHENING OF NICKEL — ALUMINIUM BRONZE DURING MULTI — STAGE AGEING PROCESS

STOPNIOWE UMACNIANIE WYDZIELENIOWE BRĄZU NIKLOWO-ALUMINIOWEGO

Methods of progressive precipitation strengthening enabling to eliminate the disadvantageous γ' phase, formed during the discontinuous transition ,are presented. Elimination of γ' precipitates makes the CuNi10Al3 alloy attain very high mechanical properties. Application of the presented methods of heat treatment gives also the possibility to modify the amount, the size and the morphology of the strengthening precipitates, which enables to control the mechanical properties of the alloy.

W niniejszej pracy przedstawiono sposoby stopniowego umacniania wydzieleniowego, pozwalające na wyeliminowanie niekorzystnej fazy γ' powstającej w przemianie nieciągłej. Eliminacja tych wydzieleń γ' sprawia, że stop CuNi10A13 uzyskuje bardzo wysokie własności mechaniczne. Zastosowanie przedstwionych sposobów obróbki cieplnej daje także możliwość wpływania na ilość, wielkość oraz morfologię wydzielań umacniających. Pozwala to na sterowanie własnościami mechanicznymi stopu.

1. Introduction

Increasing demand for modern materials with high mechanical properties and the wide range of application results from the development of science and technology.To these materials there belong the precipitation strengthened CuNiAl alloys, characterized by very high plastic formability in the supersaturated state, ability for high precipitation hardening as well as high corrosion resistance. In the course of precipitation hardening of CuNiAl alloys there appear the precipitations of γ' phase $(Cu, Ni)_3$ Al as a result of the continuous as well as the discontinuous transition [1-6]. In alloys containing not more than 11 wt % of nickel also the β phase (Cu, Ni) Al precipitates [3, 4, 6].

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In the present study the authors attempt to find the answer to the question how a saturated nickel and aluminium solution in copper reacts to a thermal stimulus (temperature) and a mechanical stimulus (deformation) in the course of precipitation (hardening) during two-stage thermal and thermal-mechanical treatment. To what degree and to what extent of the interaction of internal and external factors does the alloy react to the control of the precipitation processes which guarantee a high degree of the mechanical properties. For this reason such a method of thermal and thermal — mechanical treatment was applied which should change the precipitation kinetics so as to eliminate or to limit to a great extent the formation of γ' precipitates during discontinuous transition. The presence of these has a disadvantageous effect on the mechanical properties of the alloys.

2. Investigation method

Investigation was carried out on an alloy of the following chemical composition: 10 wt % of nickel, 3 wt % of aluminium, the rest was copper. The alloy was obtained by the method of vacuum metallurgy from components of 99.99% purity. Figure 1 shows the schemes of the applied methods of heat treatment of the alloy. The heat treatment comprising two — stage ageing (scheme *A*) consisted in the homogenization of the alloy at 950°C, quenching to 700°C and ageing at this temperature for 100 minutes. At the second stage of ageing the alloy was subjected to annealing at 500°C. The heat treatment according to scheme *B* consisted in the quenching of the alloy up to 700°C and ageing at this temperature for 100 minutes, then subsequent cooling in water. The cool alloy was subjected to 40% deformation and next to ageing at 500°C.

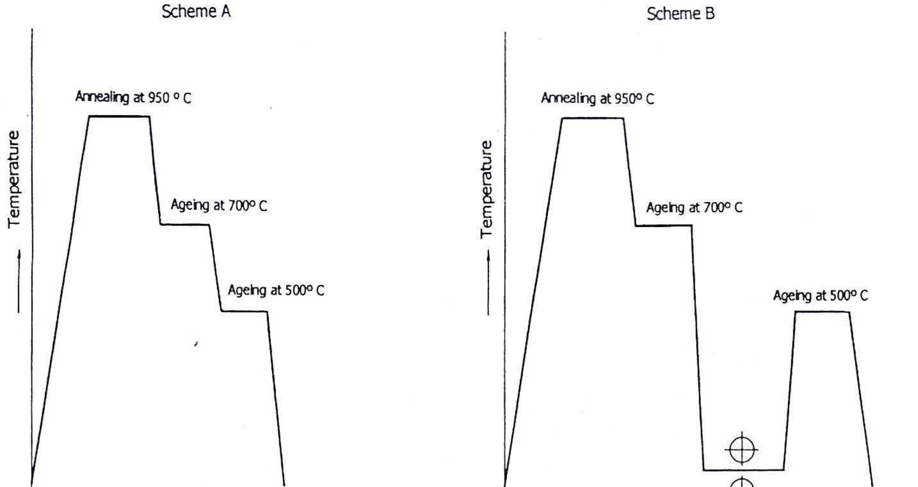


Fig. 1. Schemes of the applied methods of heat treatment and thermomechanical treatment

3. Investigation results

During heat treatment of CuNi10Al3 alloy according to scheme *A*, at the first stage of ageing, i.e. at the temperature 700°C, as a result of continuous transition, the γ' (Cu, Ni)$_3$ Al precipitates of spherical shape are formed. After 10 minutes of ageing the γ' precipitates begin to change their morphology from spherical into cubic, with the diameter attaining about 60 nm (Fig. 2). Longer ageing causes their farther growth. After 100 minutes of ageing their size is about 160 nm. At this stage of ageing also the precipitation of β (Cu, Ni) Al phase takes place (Fig. 3).The precipitates of this phase are not numerous and are located at the grain boundaries in the form of large, often oblong precipitates, with the greater dimensions reaching up to 1300 nm.

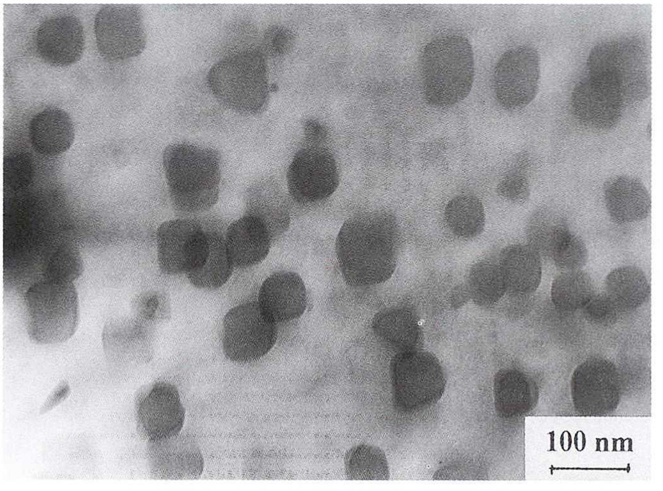


Fig. 2. Structure of CuNi10Al3 alloy, supersaturated at 700°C and aged at this temperature for 10 minutes

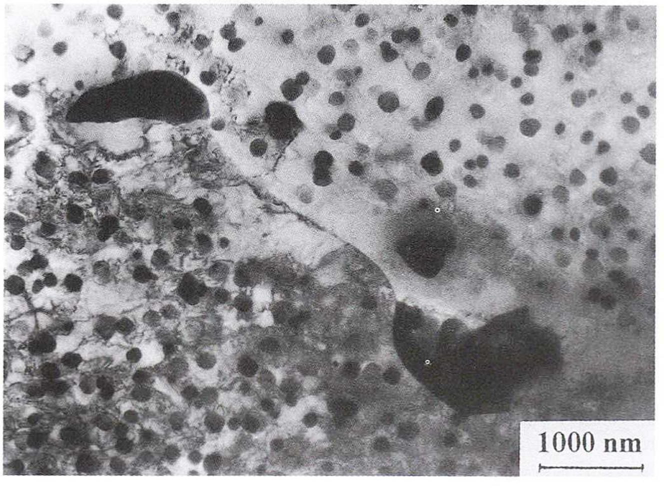
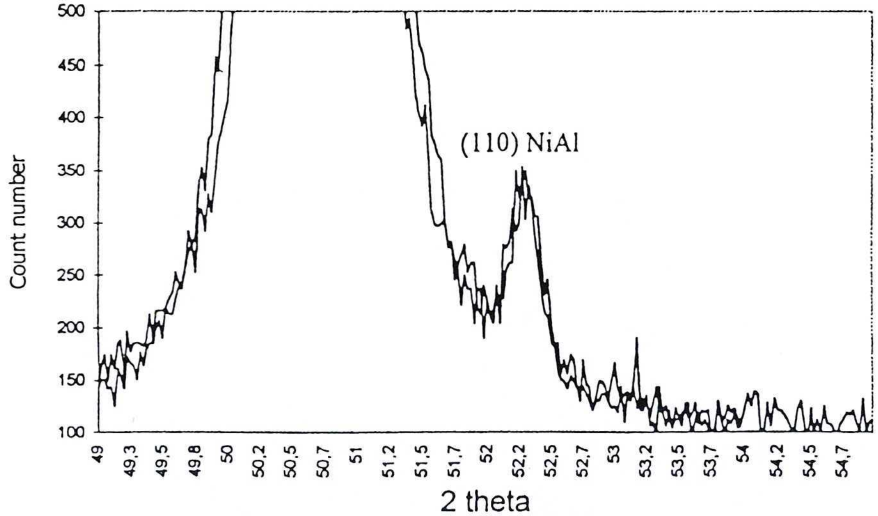
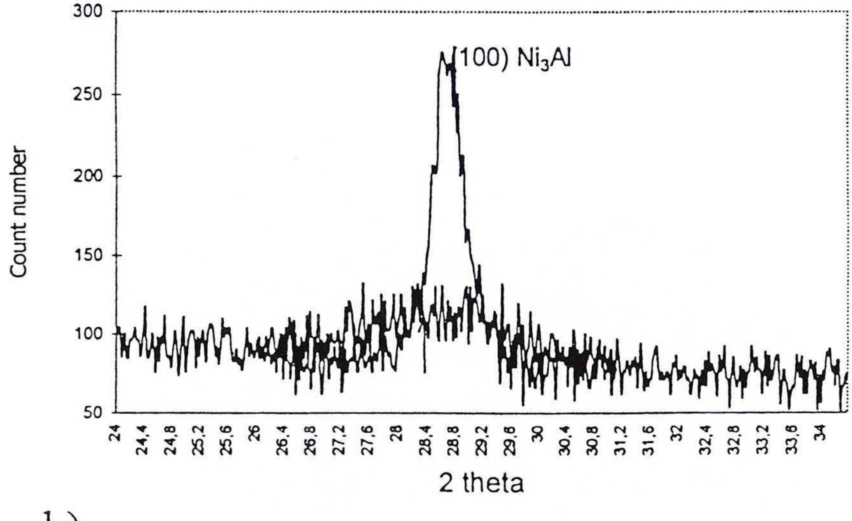


Fig. 3. Structure of CuNi10Al3 alloy, supersaturated at 700°C and aged at this temperature for 100 minutes

Investigations by X – ray diffraction were also carried out, the results of which are documented by the precipitates of γ' and β phases in CuNi10Al3 alloy aged at 700°C (Fig.4).



a)



b)

Fig. 4. X – ray diffraction of CuNi10Al3 alloy, aged at 700°C for 100 minutes: a) peak of (110) NiAl phase, b) of (100) Ni_3 Al

EDS analysis of the chemical composition of β precipitates has shown that they are built of 30–42 at % of Ni, 32–40 at % of Al. and 18–32 at % of Cu. The ratio of the content of nickel to aluminium in these precipitates is close to zero. At the grain boundaries there occur sporadically the precipitates of γ' phase, formed as a result of discontinuous transition.

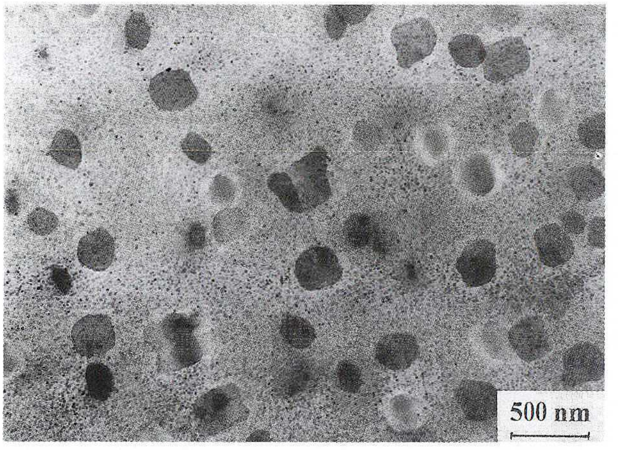


Fig. 5. Structure of CuNi10Al3 alloy, supersaturated at 700°C, aged at this temperature for 100 minutes, next aged at 500°C for 500 minutes

At the second stage of ageing, conducted at the temperature 500°C, intensive precipitation of small particles of γ' phase with 15nm diameter was observed in the whole volume of the alloy (Fig. 5). Simultaneously, the γ' precipitates of the continuous transition, formed at the first ageing stage, have grown so much that their diameters exceeded 200 nm. Long — lasting ageing of CuNi10Al3 alloy leads to coalescence of the growing γ' precipitates. As the result of this phenomenon the particles which formed agglomerations of very complex shape joined together (Fig. 6)

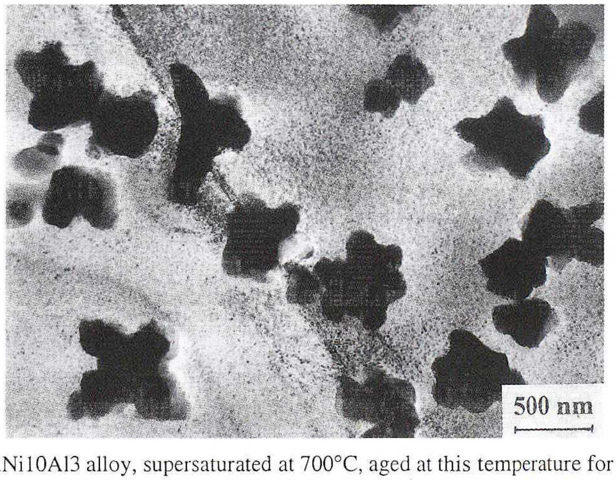


Fig. 6. Structure of CuNi10Al3 alloy, supersaturated at 700°C, aged at this temperature for 100 minutes and next aged at 500°C for 500 minutes

The performed X – ray analysis of the chemical composition of a sample surface of CuNi10Al3 alloy after two-stage ageing has been presented in the form of a „map" (Fig.7). The analyzed area (Fig. 7a) comprises a few precipitates of γ' phase formed in continuous transition. Figures 7 b, c, d show the presence of Ni, Al and Cu, respectively, in these precipitates. On the other hand the point quantitative chemical analysis of γ' phase has shown that its composition is as follows: 41–46 at % of Ni, 19–21 at % of Al and about 40 at % of Cu.

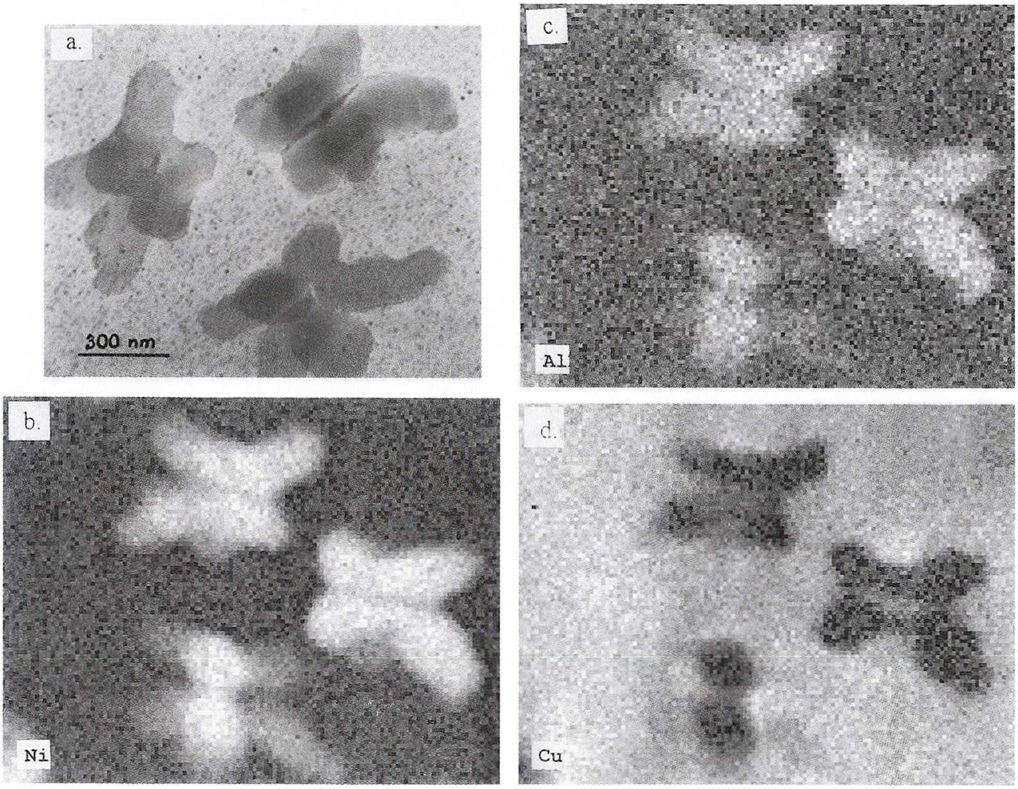


Fig. 7. X – ray analysis of the chemical composition of γ' phase in the form of a „map" of CuNi10Al3 alloy after two — stage ageing

The course of changes in the mechanical properties of CuNi10Al3 alloy at the second stage of ageing is shown in Fig. 8. The heat treatment carried out according to scheme A causes that at the second stage of ageing (after 3000 minutes), the alloy attains the following mechanical properties: $R_{0.2} = 590$ MPa, $R_m = 810$ MPa, $HV = 270$ and $A_5 = 12\%$.

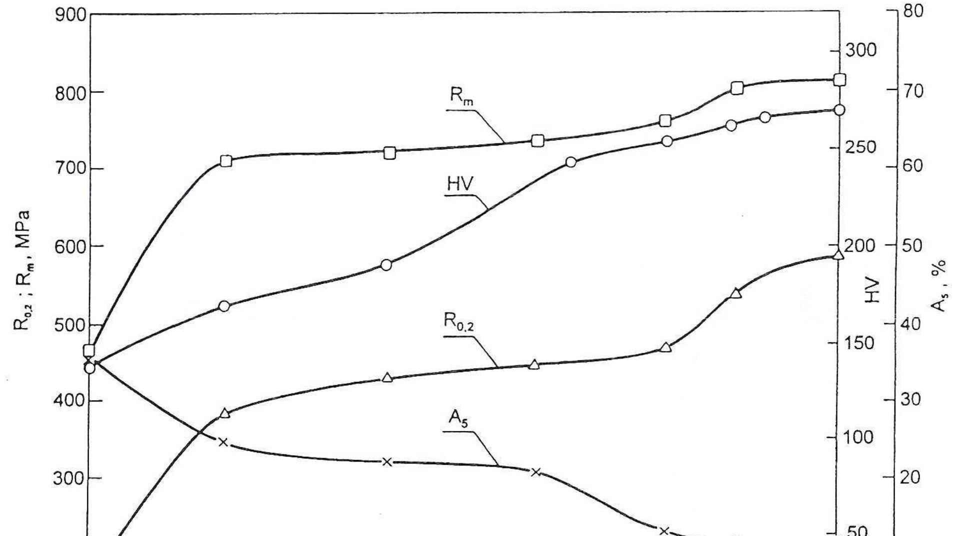


Fig. 8. Changes in the mechanical properties of CuNi10Al3 alloy, supersaturated at 700°C, aged at this temperature for 100 minutes, and next aged at 500°C

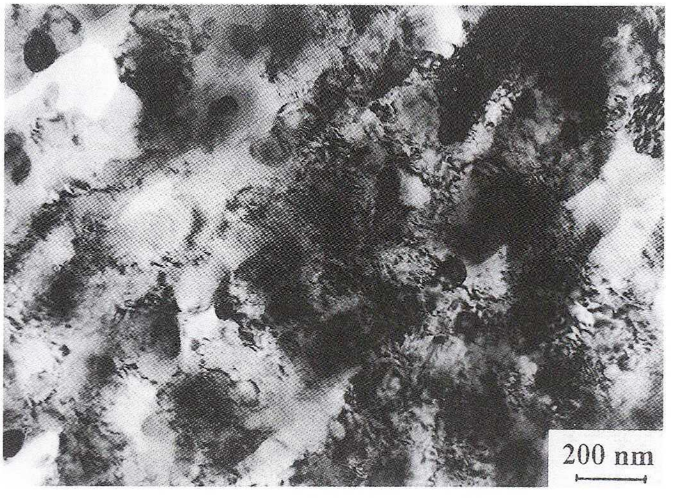


Fig. 9. Structure of CuNi10Al3 alloy, supersaturated at 700°C, aged at this temperature for 100 minutes and 40% deformed

CuNi10Al3 alloy heat treated according to scheme *B*, was quenched at 700°C and aged at this temperature for 100 minutes, then cooled in water. The structural changes which followed were identical with those which occured during the first stage of ageing according

to scheme A. Cold plastic deformation by rolling (ε = 40%) of such an alloy caused the generation of a great number of dislocations and formation of slip and shear bands. There occured also the processes of dynamic recovery (Fig. 9).
The alloy strengthened in that way (by precipitation and deformation) was aged at 500°C. During this treatment the structural inhomogeneities formed in the process of the alloy deformation became the privileged places for the nucleation of the precipitates of β phase (Fig. 10). The size of β precipitates formed at this stage of ageing is smaller (from 120 to 230 nm)than that of the precipitates formed at the first high temperature stage of ageing. Great amounts of fine γ' precipitates of the continuous transition are also observed.

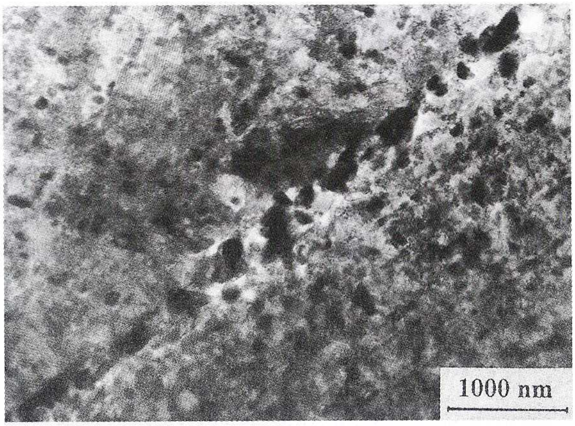


Fig. 10. Structure of CuNi10Al3 alloy, supersaturated at 700°C, aged at this temperature for 100 minutes, 40% deformed and next aged at 500°C for 500 minutes

The change in the mechanical properties of CuNi10Al3 alloy, supersaturated at 700°C, aged at this temperature for 100 minutes, cold deformed by 40% and next aged at 500°C, is shown in Fig. 11. Ageing at this temperature for 500 minutes resulted in obtaining very high strength properties. The values of these properties are as follows: $R_{0,2}$ = 1000 MPa, R_m = 1100 MPa, HV = 330.

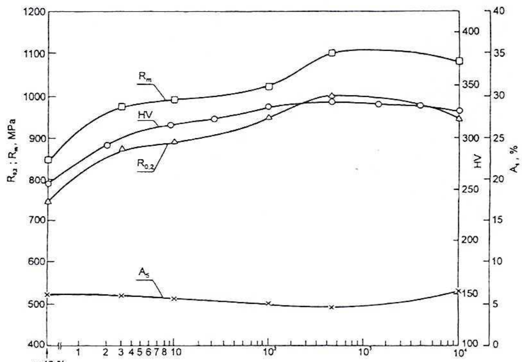


Fig. 11. Changes in the mechanical properties of CuNi10Al3 alloy, supersaturated at 700°C, aged at this temperature for 100 minutes, 40% deformed and next aged at 500°C

4. Discussion

The presented investigation results indicate that when applying the appropriate method and definite temperature-time parameters of heat treatment and thereby changing the conditions of the process, it is possible to modify the amount, morphology and distribution of precipitates of a certain type, thus materials with desired mechanical properties can be obtained.

Preliminary, high temperature ageing at 700°C (just below the solvus line) of CuNi10Al3 alloy of low degree of supersaturation prevented the occurrence of the discontinuous transition, whereas the γ' precipitates were generated in the continuous transition. High temperature induced their rapid growth in the course of ageing. The morphology of γ' precipitates was also changed from the spherical into cubic. Such a change in the morphology of the particles of a precipitated phase during ageing was also observed in Ni — Al, Ni — Si, CuNi13Al3 alloys [7, 8]. The change in the shape of the precipitates occurring during high temperature ageing may be due to the fact that the chemical composition of the precipitates became similar to the equilibrium composition. It is connected with the increase of the parameters of the mismatch of the matrix network and precipitates. Such a process in a matrix with anisotropic elastic properties induces a change of the morphology of the precipitates. The change of the morphology of γ' phase takes place whereas the same type of the structure is retained. In the course of the alloy ageing some large precipitates of β phase (Cu, Ni) Al were observed. Nucleation of β precipitates proceeds in a heterogenous way, hence the β phase was located near the grain boundaries.

The second stage of ageing at lower temperature (500°C) caused intensive precipitation of γ' phase of great dispersion. At this stage of ageing there took place further coagulation of γ' precipitates, formed during first, high temperature ageing. It is a diffusive increase of precipitates with simultaneous dissolution in the matrix of small particles of the γ' phase formed during the second stage of ageing. Overageing of CuNi10Al3 alloy caused coalescence of precipitates which formed agglomerations of very complex shapes. This second stage of ageing introduced a strong component to the total strengthening.

As a result of the application of two – stage ageing precipitation in the discontinuous transition did not occur. This fact caused that CuNi10Al3 alloy attained high strength properties with good deformability.

Application of thermomechanical treatment (scheme *B*) has led to very great hardening of CuNi10Al3 alloy as a result of precipitation and deformation strengthening. During the heat treatment, according to this scheme, the plastic deformation of the alloy was proceded by high temperature ageing at 700°C, the same as that applied during heat treatment according to *A* scheme. Accordingly, the structural changes occuring in the material at this stage of ageing are identical with those in the alloy after *A* heat treatment. The discontinuous transition did not occur in the alloy, thus it was free from the cellular precipitates, which form at the grain boundaries.Hence the material retained high plastic deformability. Introduced 40% deformation of the material induced the occurence of a great amount of dislocations and the slip and shear bands. The number of potential heterogenic nucleation areas increased. In the course of deformation there occured also the processes of dynamic recovery. After the processes of precipitation and deformation the alloy subjected to the second stage of ageing at 500°C was greatly strengthened. The distribution and the size of both β and γ' precipitates were changed. Phase β precipitates in a great amount and was located chiefly in the shear bands. These precipitates are smaller than those formed in the grain boundaries during preliminary ageing, whereas the main strengthening phase γ', formed in the continuous transition, precipitated in a great amount in the form of very small, spherical particles. This enabled to obtain maximal strengthening. The structure of CuNi10Al3, formed as a result of two – stage ageing, separated by plastic deformation, allowed to obtain material with very high strength properties.

5. Conclusions

- High mechanical properties of CuNi10Al3 alloy are obtained when the work hardening process is carried out in such way as to eliminate the presence of the γ' precipitates of the discontinuous transition. This can be realized applying two – stage heat treatment (scheme *A*). The alloy attains then the following mechanical properties: $R_{0,2}$ = 590 MPa, R_m = 810 MPa, HV = 270, A_5 = 12 %
- Very high strength properties in CuNi13Al3 are obtained as a result of complex thermomechanical treatment (scheme *B*). Then the strength properties are as follows: $R_{0,2}$ = 1000 MPa, R_m = 1100 MPa, HV = 330.

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