ARCHIVES OF METALLURGY
Volume 48 2003 Issue 3

JANUSZ GRYZIECKI*, ANDRZEJ ŁATKOWSKI*

THE ROLE OF MICROADDITIONS IN THE KINETIC CHANGE OF PRECIPITATION DURING THE AGEING PROCESS OF NICKEL — ALUMINIUM BRONZE

ROLA MIKRODODATKÓW W ZMIANIE KINETYKI WYDZIELANIA STARZONEGO BRĄZU NIKLOWO — ALUMINIOWEGO

The paper presents a method which allows to eliminate the γ' (Cu, Ni)$_3$Al phase of discontinuous transition occurring during ageing of CuNi10Al3 alloy. Introduction of additions such as Si or Ti in the amount of some tenths of percent into CuNi10Al3 alloy causes that γ' phase of the discontinuous transition is not precipitated. CuNi10Al3 alloy, free from the lamellar γ' precipitates, formed in the discontinuous transition, attains very high strength properties and good deformability.

W niniejszej pracy przedstawiono sposób pozwalający na wyeliminowanie fazy γ'(Cu, Ni)$_3$Al przemiany nieciągłej powstającej podczas starzenia stopu CuNi10Al3. Wprowadzenie do stopu CuNi10Al3 dodatków w postaci Si lub Ti w ilościach dziesiątych części procentu powoduje, że nie wydziela się faza γ' przemiany nieciągłej. Stop CuNi10Al3 pozbawiony płytkowych wydzieleń γ' tworzących się w przemianie nieciągłej uzyskuje bardzo wysokie własności wytrzymałościowe oraz dobrą odkształcalność.

1. Introduction

Nickel aluminium bronze shows great tendency for precipitation strengthening which offers the possibility to obtain materials of high strength properties. An additional advantage is their high ability to plastic deformation in supersaturated state and corrosion resistance. In the course of their ageing, as a result of continuous and discontinuous transition the γ' (Cu, Ni)$_3$ Al phase is formed, and in alloys containing not more than 11 wt % of Ni – the β (Cu, Ni) Al phase [1–5]. This phase is a secondary solution with A 2 lattice. The β precipitates are incoherent and they nucleate in a heterogenic way. They are located mainly near the grain boundaries, forming large, oval particles. As a result of discontinuous

* WYDZIAŁ METALI NIEŻELAZNYCH, AKADEMIA GÓRNICZO-HUTNICZA, 30-059 KRAKÓW, AL. MICKIEWICZA 30

transition fine, spherical γ' precipitates are formed, while the discontinuous disintegration is responsible for the formation of lamellar precipitates of this phase. The γ' precipitates are coherent and they strengthen the alloy. They are characterized by the ordered structure $L1_2$ [6, 7]. The lamellar precipitates of γ' formed in the discontinuous transition are found near the grain boundaries. These are the nucleation sites of microcracks during plastic deformation of the alloy, whose propagation leads to destruction of the material. Elimination or a considerable limitation of the occurrence of this undesirable phase should improve the mechanical properties of the alloy. The methods enabling to eliminate γ' precipitates formed during discontinuous transition are the step – like ageing or introduction of appropriate microadditions in to the alloy. The effectiveness of the application of gradual ageing in Cu – Ni – Al alloys was discussed in the study [8]. The aim of the presented investigations was the elimination of γ' precipitates formed in the discontinuous transition by introducing into CuNi10Al3 alloy the microadditions such as Si or Ti, or Nb in the amount of some tenths of percent.

2. Investigation methods

Investigations were carried out on an alloy containing 10 wt % of nickel, 3 wt % of aluminium, the rest was copper. To the alloy of the above composition the fourth component was added as a microaddition of Si, or Ti or Nb. Each microaddition was introduced in the amount of 0.4 wt %. The alloys were prepared using the technique of vacuum metallurgy, from components of 99,99% purity. The cast alloys were homogenized at the temperature 950°C, supersaturated in water and next cold rolled. The hardened alloys were annealed again at the temperature 950°C and water quenched. Ageing was carried out in a salt – bath furnace at the temperature 500°C for various time periods. Thermo-mechanical treatment was also applied in which the supersaturated alloy was subjected to deformation ($\varepsilon = 40\%$) by rolling, and next to ageing at the temperature 500°C. The degree of hardening was defined by measuring the mechanical properties obtained in the tension or hardness tests. Structural investigations were carried out using an optical and an electron microscope.

3. Investigation results

CuNi10Al3 alloy with Si addition, aged at the temperature 500°C becomes hardened after 10 min. long incubation. After that time the hardening increases quickly. The process of strengthening of the alloy is illustrated in Fig. 1 by the dependence of the change in the mechanical properties as a function of the ageing time. After 10 min. ageing the hardening of the alloy is high and its mechanical properties are as follows: $R_m = 710$ MPa, $R_{0.2} = 545$ MPa, HV = 258, $A_5 = 23\%$. The hardening is induced by the precipitates of γ' $(Cu, Ni)_3$ Al phase, formed in the continuous transition, which occur in the form of very small, spherical particles. Their size, after 10^4 minutes of ageing, equals 10 nm (Fig. 2). At the grain boundaries there appears also the β(Cu, Ni)Al phase. These are large, oval precipitates with the larger size from 100 to 300 nm (Fig. 3). At the grain boundaries and inside the grains there are also found the precipitates of Ni_3Si phase (Figs 2 and 4). EDS analysis of the chemical composition of these precipitates has shown that they are built of 45 ÷ 51 at % of Ni and 14 ÷ 18 at % of Si. The ratio of Ni to Si content in these particles was 3 : 1.

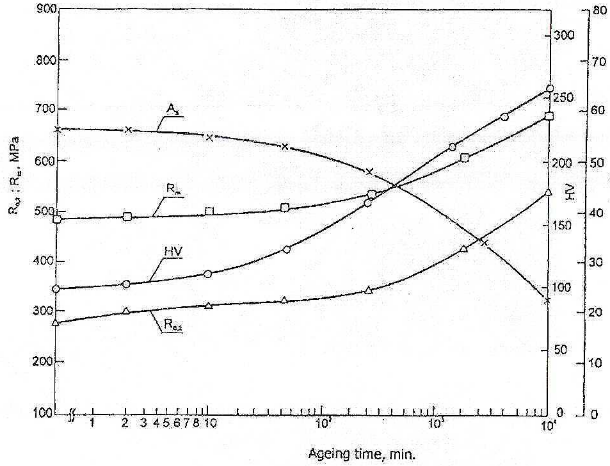

Fig. 1. Change of the mechanical properties with the ageing time of CuNi10Al3 alloy with 0.4 wt % addition of Si, homogenized at 950°C, water quenched and aged at 500°C

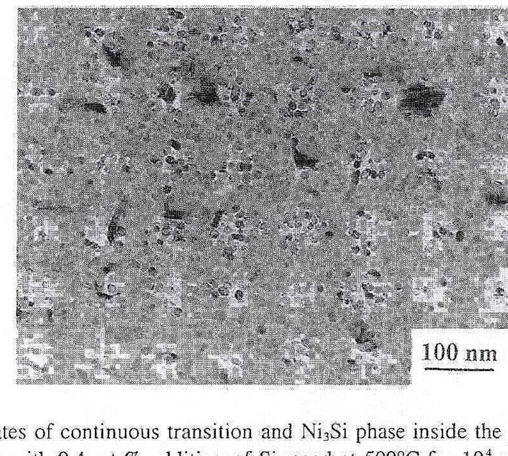

Fig. 2. γ' precipitates of continuous transition and Ni_3Si phase inside the grains of CuNi10Al3 alloy with 0.4 wt % addition of Si, aged at 500°C for 10^4 minutes

Plastic deformation (ε = 40%) of supersaturated CuNi10Al3 alloy with Si addition caused that during its ageing the hardening of the alloy was greatly increased. Already after 10^3 minutes the maximal strengthening was attained (Fig. 5). Due to the applied thermo-mechanical treatment very high strength properties were obtained. The values of these properties were as follows: $R_m = 950$ MPa, $R_{0.2} = 875$ MPa, HV = 290. However, the deformability of the alloy became reduced, which is evidenced by the value of the percentage elongation $A_5 = 6\%$.

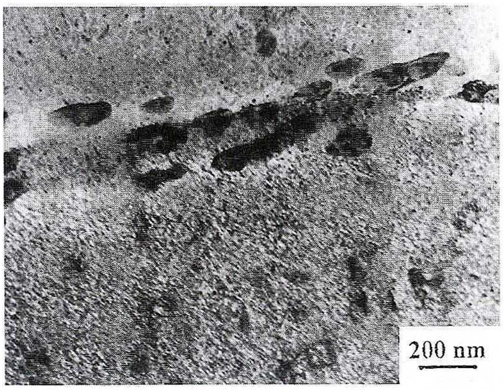

Fig. 3. Precipitates of β phase in CuNi10Al3 alloy with 0.4 wt % addition of Si, aged at 500°C for 10^4 minutes

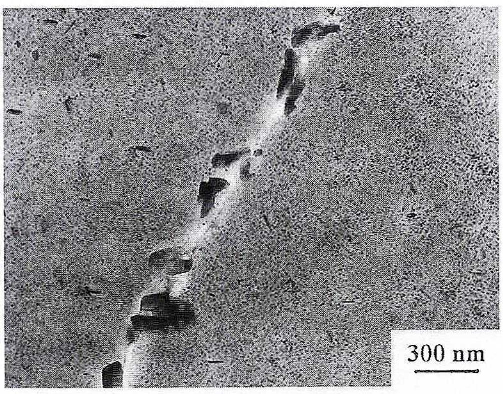

Fig. 4. Ni_3Si precipitates in grains and near the grain boundaries in CuNi10Al3 alloy with 0.4 wt % addition of Si, aged at 500°C for 10^4 minutes

Plastic deformation of the supersaturated alloy caused the deformation of structural inhomogeneity in the form of slip and shear bands, which became privileged sites of the nucleation of β phase precipitates (Fig. 6). The β phase was also formed in the remaining part of the material (Fig. 7). Moreover, within the grain boundaries and in their entire volume there appeared small Ni_3Si precipitates (Fig. 7). The ageing process induces intensive, continuous nucleation and the increase of γ' precipitates of the continuous transition in the whole volume of the material. The γ' precipitates formed as a result of continuous transition are shown in Figs 6 and 7. Observation of the structure of CuNi10Al3 alloy with Si addition shows that both after thermal as well as thermo – mechanical treatment the γ' precipitates of discontinuous transition do not occur in the alloy.

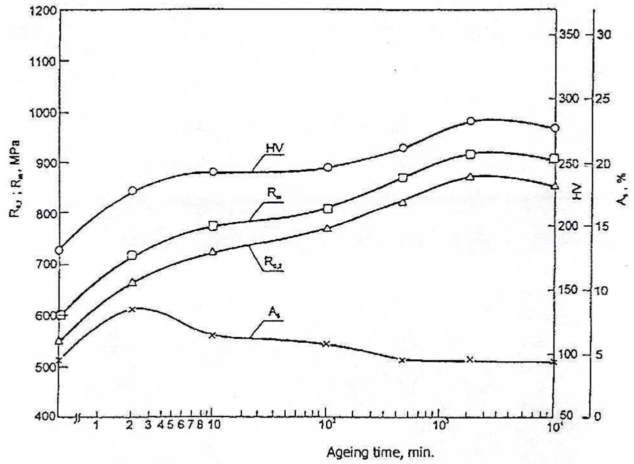

Fig. 5. Change of the mechanical properties with the ageing time of CuNi10Al3 alloy with 0.4 wt % addition of Si, homogenized at 950°C, water quenched, deformed by $\varepsilon = 40\%$ and aged at 500°C

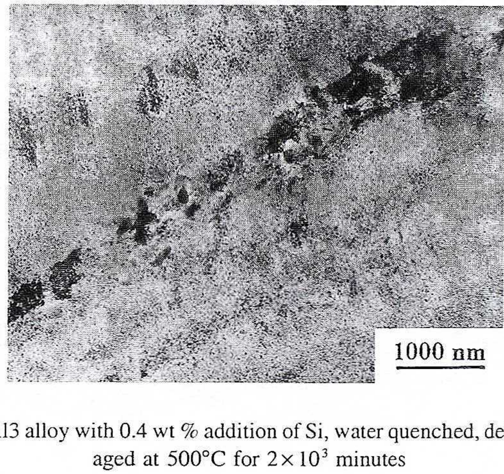

Fig. 6. Structure of CuNi10Al3 alloy with 0.4 wt % addition of Si, water quenched, deformed by $\varepsilon = 40\%$ and next aged at 500°C for 2×10^3 minutes

The other addition to CuNi10Al3 alloy, whose presence was examined with respect to the possibility of removing the γ' precipitates of discontinuous transition occurring during ageing, was titanium. The alloy with Ti addition, aged at the temperature 500°C, after a short period of incubation underwent fast, monotonic hardening. After 2×10^3 minutes of ageing the material attained the following maximal mechanical properties: $R_m = 750$ MPa, $R_{0.2} = 430$ MPa, HV = 235, $A_5 = 33\%$ (Fig. 8).

In the structure of a hardened alloy there appear in the grains very small, spherical (ϕ 7 nm) γ' (Cu, Ni)$_3$ Al precipitates (Fig. 9). The β(Cu, Ni) Al precipitates are situated near the grain boundaries (Fig. 10). They are large, oval, with the greater size reaching 170 nm. EDS analysis has shown that the grain boundaries are rich in titanium. Repeated measurements have shown that the amount of titanium in the grain boundaries attains from 10 to 15 at %, while the amount of titanium in the grains does not exceed 0.4 at %.

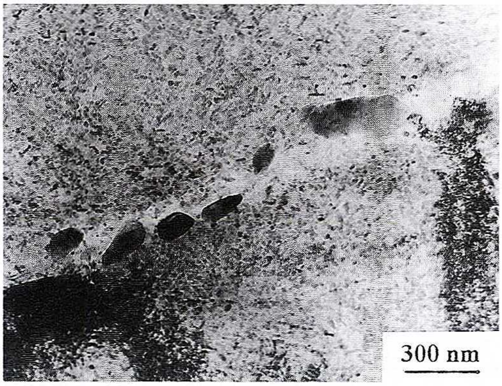

Fig. 7. Structure of CuNi10Al3 alloy with 0.4 wt % addition of Si, water quenched, deformed by ε = 40% and next aged at 500°C for 2×10^3 minutes

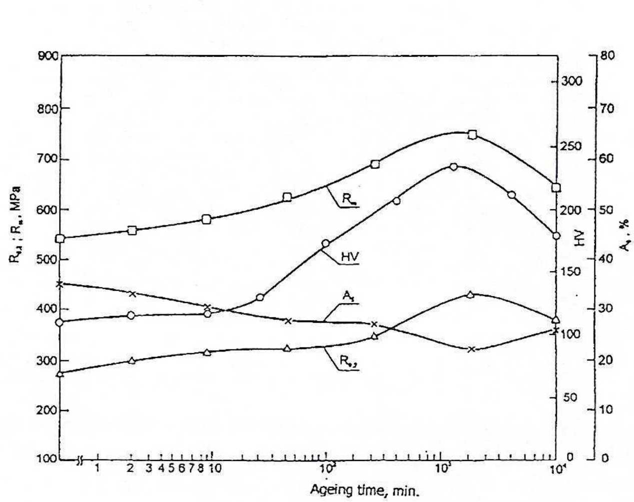

Fig. 8. Change of the mechanical properties with ageing time of CuNi10Al3 alloy with 0.4 wt % addition of Ti, homogenized at 950°C, water quenched and next aged at 500°C

Application of thermo – mechanical treatment, in which the deformation $\varepsilon = 40\%$ was used, caused considerable increase of the strength properties with simultaneous reduction of the plastic properties. Ageing for 2×10^3 minutes at the temperature 500°C caused that the alloy attained maximal hardening (Fig. 11). Its mechanical properties were as follows: R_m = 925 MPa, $R_{0.2}$ = 875 MPa, HV = 285, and A_5 = 4.5%.

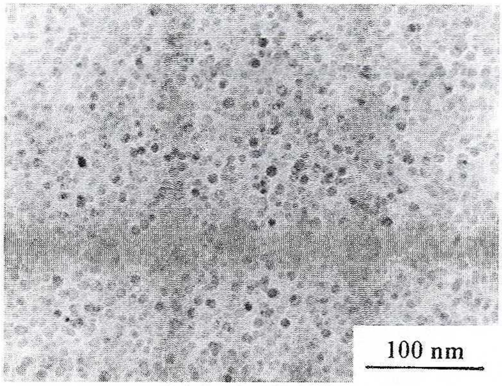

Fig. 9. γ' precipitates of continuous transition inside the grains of CuNi10Al3 alloy with 0.4 wt % addition of Ti, aged at 500°C for 2×10^3 minutes

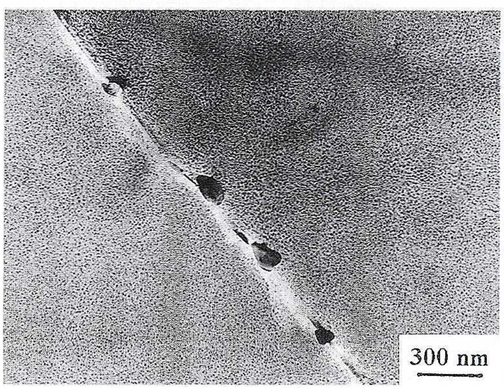

Fig. 10. Precipitates of β phase near the grain boundaries of CuNi10Al3 alloy with 0.4 wt % addition of Ti, aged at 500°C for 2×10^3 minutes

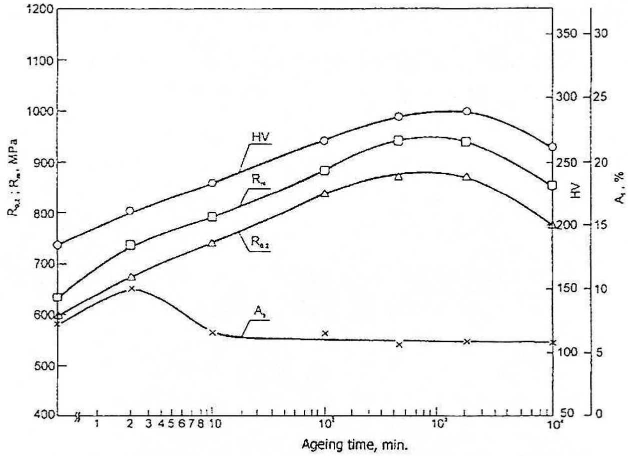

Fig. 11. Change of the mechanical properties with the ageing time of CuNi10Al3 alloy with 0.4 wt % addition of Ti, homogenized at 950°C, water quenched, deformed by $\varepsilon = 40\%$ and next aged at 500°C

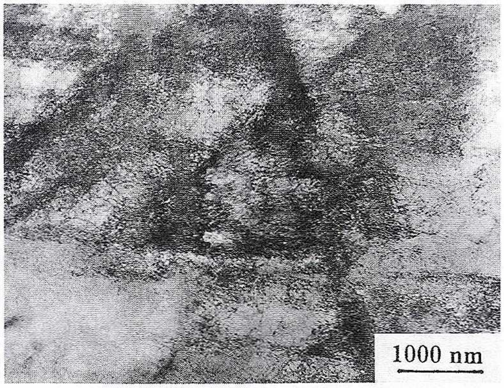

Fig. 12. Structure of CuNi10Al3 alloy with 0.4 wt % addition of Ti, water quenched, deformed by $\varepsilon = 40\%$, and next aged at 500°C for 2×10^3 minutes

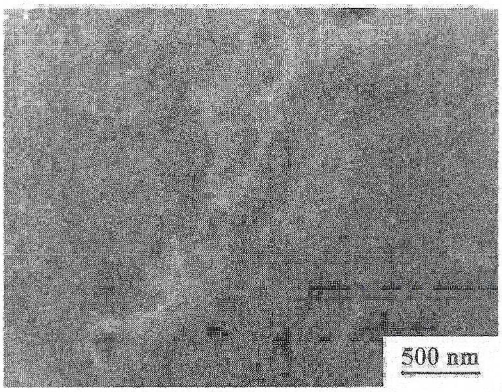

Fig. 13. Precipitates of β phase in CuNi10Al3 alloy with 0.4 wt % addition of Ti, water quenched, deformed by $\varepsilon = 40\%$, and next aged at 500°C for 2×10^3 minutes

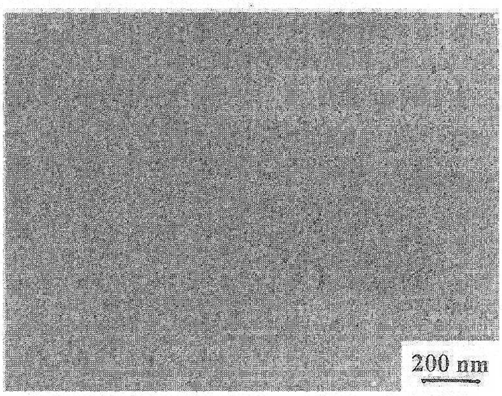

Fig. 14. Precipitates of γ' phase of continuous transition in CuNi10Al3 alloy with 0.4 wt % addition of Ti, water quenched, deformed by $\varepsilon = 40\%$ and next aged at 500°C for 2×10^3 minutes

In the structure of a deformed material, after 2×10^3 minutes of ageing there can be observed structural inhomogeneities (Fig. 12). The β phase was located both in the grain boundaries and in the grains inside (Fig. 13). The size of these precipitates was about 100 nm. In the entire volume of the alloy a great amount of small precipitates of γ' phase, formed in the continuous transition, was found (Fig. 14).

Observations by means of an optical and an electron microscope have shown that CuNi10Al3 alloy with Ti addition does not contain the γ' precipitates formed in the discontinuous transition.

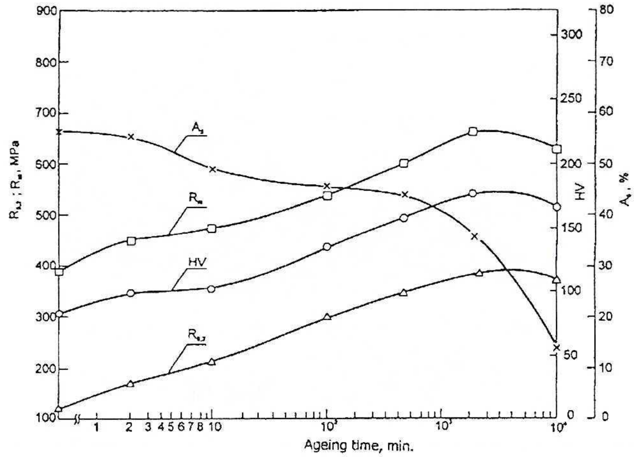

Fig. 15. Change of the mechanical properties with the ageing time of CuNi10Al3 alloy with 0.4 wt % addition of Nb, homogenized at 950°C, water quenched, and next aged at 500°C

The third, applied addition to CuNi10Al3 alloy was niobium. Its addition induced solution hardening of the alloy only to a small extent. The alloy aged at the temperature 500°C became hardened without the period of incubation, attaining the maximal strength properties after 10^4 minutes. The values of the mechanical properties after this ageing time were as follows: R_m = 670 MPa, $R_{0.2}$ = 390 MPa, HV = 178 and A_5 = 13.5% (Fig. 15).

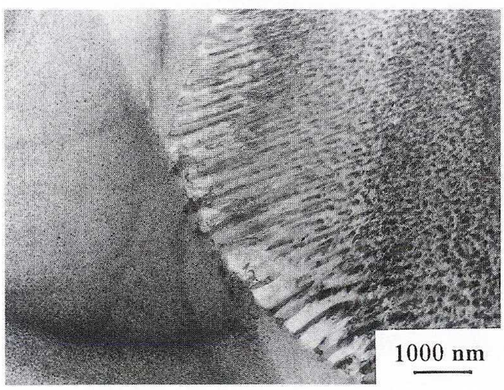

Fig. 16. γ' precipitates of discontinuous transition of CuNi10Al3 alloy with 0.4 wt % addition of Nb, aged at 500°C for 10^4 minutes

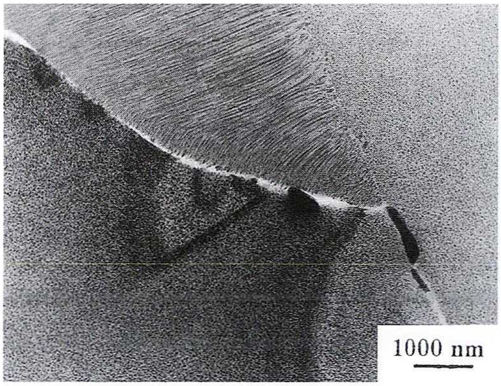

Fig. 17. γ' precipitates of continuous and discontinuous transition and β phase of CuNi10Al3 alloy with 0.4 wt % addition of Nb, aged at 500°C for 10^4 minutes

In the course of the ageing of the alloy at the grain boundaries there are formed areas migrating into their inside, built of lamellar precipitates of γ' $(Cu, Ni)_3Al$ of discontinuous transition. The thickness of these precipitates after 10^4 minutes of ageing amounts from 60 to 100 nm (Figs 16, 17). Observations of the structure by means of an optical microscope have shown that the majority of the grain boundaries of the alloy has been decorated with γ' precipitates formed in a discontinuous transition (Fig. 18). In the grain boundaries there are also visible oval precipitates of β (Cu, Ni)Al phase (Fig. 17). The inside of the grains of the aged alloy is filled with spherical γ' precipitates of continuous transition (Figs 16, 17).

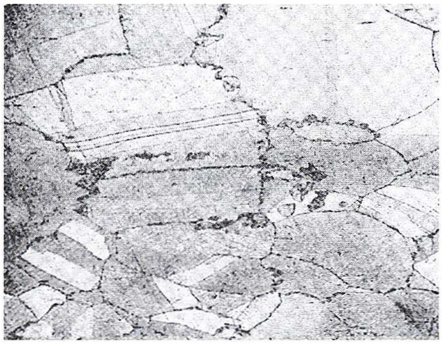

Fig. 18. Structure of CuNi10Al3 alloy with 0.4 wt % addition of Nb, aged at 500°C for 10^4 minutes. Magnified 250x

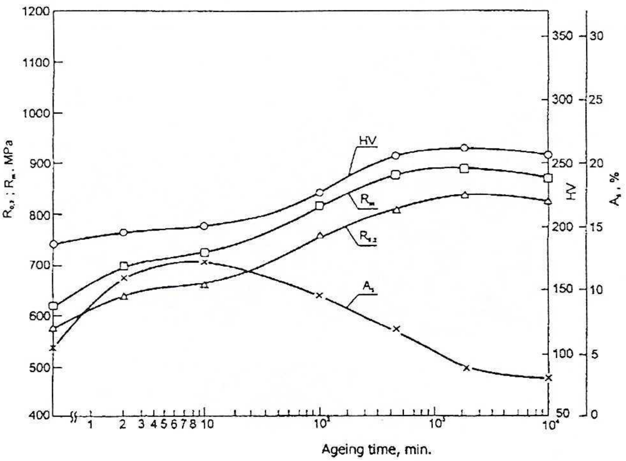

Fig. 19. Change of the mechanical properties of CuNi10Al3 alloy with 0.4 wt % addition of Nb, homogenized at 950°C, water quenched, deformed by $\varepsilon = 40\%$ and aged at 500°C

Thermo-mechanical treatment in which the supersaturated alloy was deformed by 40%, changed the progress and the effects of the strengthening process. The increase of the strength properties of the alloy, resulting from precipitation hardening, begins from a higher level. The aged alloy attains after 2×10^3 minutes the following maximal strength properties: R_m = 880 MPa, $R_{0.2}$ = 840 MPa and HV = 260. These strength properties are accompanied by low deformability (A_5 = 4%). The above changes in the mechanical properties are shown in Fig. 19.

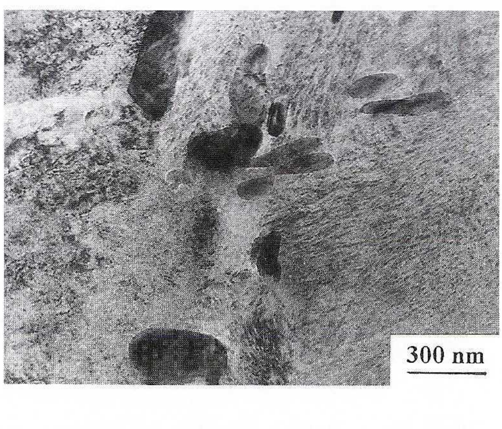

Fig. 20. Structure of CuNi10Al3 alloy with 0.4 wt % addition of Nb, supersaturated, deformed by $\varepsilon = 40\%$ and aged at 500°C for 2×10^3 minutes

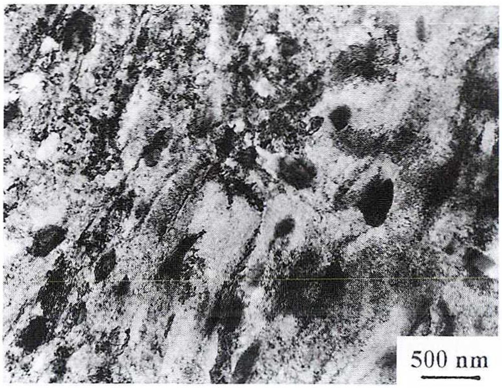

Fig. 21. Precipitates of β phase in the shear bands of CuNi10Al3 alloy with 0.4 wt % addition of Nb, water quenched, deformed by $\varepsilon = 40\%$, aged at 500°C for 2×10^3 minutes

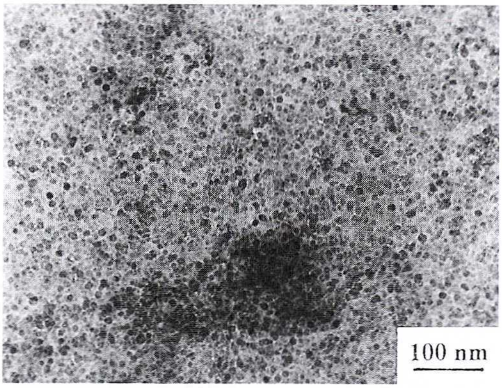

Fig. 22. Continuous precipitates of γ' phase in CuNi10Al3 alloy with 0.4 wt % addition of Nb, water quenched, deformed by $\varepsilon = 40\%$, aged at 500°C for 2×10^3 minutes

Plastic deformation ($\varepsilon = 40\%$) of the supersaturated alloy caused that on the developed structural inhomogeneities there took place intensive precipitation of the lamellar γ' phase of discontinuous transition (Fig. 20). In the shear bands there were also located the precipitates of β phase (Fig. 21). The γ' basic strengthening phase, forming in the continuous transition, occurs inside the grains in the form of very small (about 10 nm), coagulated precipitates (Fig. 22). The above presented results of structural investigations indicate that the addition of niobium to CuNi10Al3 alloy did not prevent the precipitation of the γ' phase of discontinuous transition.

4. Discussion

Introduction of alloy additions such as Si or Ti into the CuNi10Al3 alloy caused a change of the precipitation kinetics during ageing. Precipitation of γ' phase in the discontinuous transition did not occur. This is due to the fact that the progress of discontinuous precipitation takes place only on the boundaries of grains able to migrate and on subgrains formed as a result of plastic deformation. All the factors which make difficult the migration of the grain boundaries prevent or inhibit the discontinuous precipitation. Such factors are the microadditions of elements introduced into the alloy which become segregated to the grain boundaries, or form new phases, for which the grain boundaries are the privileged sites of nucleation. Introduction of Si into CuNi10Al3 alloy caused the formation of Ni_3Si phase whose precipitates became located both at the boundaries of grains and in their inside. It is to be assumed that the presence of these precipitates near the boundaries was responsible for their inactivation so that they could not become the nucleation sites for the precipitates of discontinuous transition. On the other hand, the Ti addition to the alloy caused great segregation of this element to the grain boundaries. The grain boundaries became inactivated by the Ti atoms. The boundaries, inactivated in this way, did not become the sites of the formation of discontinuous precipitates.

It should be also taken into consideration that the possibility of the occurrence of a discontinuous transition may be also determined by the value of the driving force of this reaction. For the decomposition to occur as a result of discontinuous transition the driving force must remain unchanged throughout, the time, ie continuous precipitation cannot proceed in a competitive mode before the transition front. If microadditions which favour the process of nucleation of continuous transition are introduced into the alloy, formation of precipitates of this transition caused impoverishment of the solution in the supersaturated component. This competitive precipitation process reduces the driving force of the reaction of discontinuous transition, preventing or inhibiting its occurrence. The microadditions, such as Si or Ti, introduced into CuNi10Al3 alloy, undoubtedly influenced the formation of the continuous precipitates of γ' $(Cu, Ni)_3Al$. Their addition caused that γ' precipitates of the continuous transition were numerous, and were of small size.

Niobium introduced into CuNi10Al3 alloy did not cause the inactivation of the grain boundaries. The investigation results indicate that no niobium phases were formed in the grain boundaries and no segregation of niobium to the grain boundaries was observed. Hence, the addition of niobium to the alloy did not stop the discontinuous transition.

5. Summarizing remarks

Introduction of alloy additions such as Si or Ti in the amount of 0.4 wt % into CuNi10Al3 alloy causes a delay in the precipitation of the main strengthening phase γ' occurring in the continuous transition. This can be observed on the ageing curves of the examined alloy as the occurrence of the incubation period (Figs 1, 8). Small precipitates of Ni_3Si phase, situated in the grain boundaries, or a strong segregation of Ti atoms to the grain boundaries prevent the nucleation and afterwards the growth of the cellular precipitates of γ' occurring in the discontinuous transition. Elimination of γ' precipitates of discontinuous transition causes that the alloy attains high strength properties, while retaining good deformability. The alloy additions, such as Si or Ti, introduced into the alloy, which was deformed after supersaturation, not only prevent the occurrence of γ' precipitates of the discontinuous transition, but also inhibit the processes of recovery and recrystallization in the course of ageing, and are responsible for the very high strength properties. The obtained strength properties of CuNi10Al3 alloy with Si or Ti additions after thermo-mechanical treatment allow to place it among materials of the highest strength properties which can be obtained in copper based alloys.

Application of niobium as an addition to CuNi10Al3 alloy does not eliminate γ' precipitates of discontinuous transition, the consequence of which are lower strength properties and lower deformability.

Acknowledgements

The work was realized in the frame of grant project – Committee of Scientific Research (KBN) , No. 4 T08 B04322.

REFERENCES

[1] W. Leo, G. Wasserman, Metall. **22**, 10 (1967).
[2] M. Miki, Y. Amano, Trans. JIM, **20**, 1 (1979).
[3] J. Gryziecki, Z. Sierpiński, A. Łatkowski, Arch of Metall. **40**, 437 (1995).
[4] Z. Sierpiński, J. Gryziecki, Zeitschrift für Metallk. **89**, 551 (1995).
[5] Z. Sierpiński, Doctoral thesis (in Polish), Academy of Mining and Metallurgy, Kraków, 1998.
[6] H. Tsuda, T. Jto, Y. Nakayama, Scripta Metall. **20**, 1555, 1996.
[7] Y-R. Cho, Y-H. Kim, T. D. Lee, Journal of Met. Science, **26**, 2879, 1991.
[8] J. Gryziecki, A. Łatkowski, Archives of Metall., (in print).

REVIEWED BY: STANISŁAW WIERZBIŃSKI
Received: 2 June 2003.