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Precipitation process of the Ni_3Al phase in copper-based alloys

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Materials

ABSTRACT

Purpose: This research was aimed to investigate the mechanism of Ni_3Al phase precipitation during long-term process of ageing Cu-Ni-Al. type alloys with particular account of the precipitates morphology changes, including the changes in their size with varying temperature and ageing time, so as to determine an effect of the elastic strain energy on these changes.
Design/methodology/approach: Samples of cold-rolled strips from the CuNi16Al5 alloy were solution – treated at 900°C for 1h in argon atmosphere, water quenched and next aged at the temperatures of 450 and 550°C for up to 380 and 760 hours, respectively. Their microstructure was investigated by transmission electron microscopy.
Findings: It was found that decomposition of supersaturated solid solution proceeds by nucleation and growth of the coherent precipitates of the $L1_2$ –Ni_3Al phase. Their morphology changes as a result of competitive influence of an elastic strain energy, surface energy on the matrix-precipitate inter-phase boundary, and the energy of elastic interaction between precipitates. The $L1_2$ –Ni_3Al precipitates nucleate as the spherical ones and grow, forming intermediate sub-structures, until they reach a cubic form with the planes parallel to the{100} planes of a matrix and take privileged positions along the <110> directions. Clear deviations from the LSW coagulation theory and its modifications, demonstrated by the slow-down of the process, have been observed. In the extreme case, growth of the precipitates can be completely stopped in some time ranges of the ageing process.
Research limitations/implications: Further research should be concentrated on the precipitation kinetics within a wider range of volumetric fraction of the Ni_3Al phase in a copper matrix.
Practical implications: This effect can be used in practice to stabilise mechanical properties at elevated temperature.
Originality/value: The paper contributes to better understanding of the precipitation mechanism in the alloys examined.
Keywords: Metallic alloys; Electron microscopy; Precipitation hardening; Morphology

1. Introduction

It is well known that inter-metallic phase particles with the $L1_2$ –Ni_3Al structure are being precipitated in the aged Ni-based super-alloys during homogeneous decomposition of the supersaturated solid solution [1-3]. Earlier investigations into this process indicated the role of elastic strain energy and its effect on the mechanism and kinetics of the precipitation of this phase. It was found that clear deviations from coagulation theory [4,5] and its modifications [6-8] take place in precipitation systems situated in elastic strain field. The $t^{1/3}$ relation [1] appeared not to be met there, which evinced itself by a slow-down of coagulation process, accompanied by a standard deviation decrease, which indicated that sizes of particular precipitates become increasingly homogeneous and the microstructure tends to a particular state.

It has been shown in our previous works [9,11] and in a work [12] that the $L1_2$ –Ni_3Al phase particles are also precipitated during processes of homogeneous decomposition of supersaturated solid solution in the Cu-Ni-Al based alloys. As it was proved, this was non-equilibrium phase in these alloys (CuNi15Al5, Cu(Ni+Fe)15Al5, CuNi7Al2), whereas the B2-NiAl phase was the equilibrium one. Therefore, this work was aimed to investigate the mechanism of Ni_3Al phase precipitation during long-term process of ageing Cu-Ni-Al type alloys with particular account of the precipitates morphology changes, including the changes in their size with varying temperature and ageing time, so as to determine an effect of the elastic strain energy on these changes.

2. Experimental

This work was carried out with an experimental CuNi16Al5 alloy, whose chemical composition was (wt %): Ni – 16,52; Ni – 5,14; Cu – balance. The specimen, cut from the cold rolled strips, 0,3 mm in thickness, were solution – treated at 900°C for 1h in argon atmosphere, water quenched and next aged at the temperatures of 450 and 550°C for up to 380 and 760 hours, respectively. The microstructure was investigated by JEOL's JEM 2000 FX transmission electron microscope, operating at 160 kV. Disc samples for TEM observations were electro-polished at 35°C in an electrolyte consisting of 33 % nitric acid and 67 % methanol in a Struers twin-jet electro-polisher.

3. Results and discussion

Fig. 1a shows typical microstructure of an alloy aged for 24 hours and a typical SAD pattern (it should be pointed out that this pattern was representative for all the samples examined, also for those aged at 550^0C). Randomly distributed, spherical, coherent precipitates, 10 nm in average diameter (Fig 1b), are seen. The SAD patterns have shown that these precipitates belong to the $L1_2$ – Ni_3Al phase and an orientation relationship between Ni_3Al precipitates and the matrix is cubic.

During coarsening by further aging at 450^0C, the shape of the precipitates did not change, similarly as their distribution within the whole alloy volume. Only their size has changed, but to the limited extent. These changes are illustrated by the exemplary microstructure images shown, together with precipitate size distributions, in Fig. 1a – 1f.

Results of the measurements have been summarised in a diagram (Fig. 2), illustrating the changes of an average precipitate diameter together with standard deviation in dependence on ageing time at the temperature of 450°C.

Ageing of the alloy under investigation only at the temperature of 450°C for up to 380 hours did not allow to investigate the whole cycle of changes of morphological features of the Ni_3Al phase precipitates in a copper matrix. For that reason, ageing temperature was elevated to 550^oC and the ageing time to 760 hours. The results obtained are presented in Figs 3 and 4. Morphological changes in the precipitates are shown in the left columns, and the quantitative changes in a form of precipitates volume distributions – in the right columns. The summarised results of precipitates size measurements in dependence on ageing time, grouped by particular precipitate fractions (spherical, cubic), have been illustrated in Fig. 5. As a common measure of a size of the spherical and cubic precipitates, their volumes have been taken.

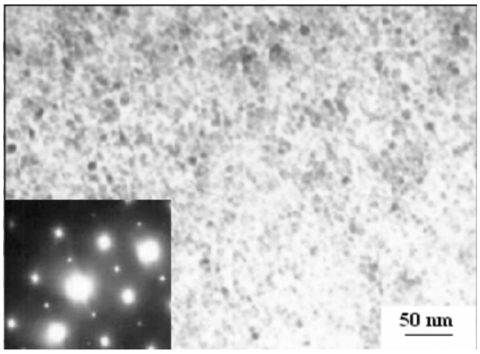
It can be concluded from the figures presented above that the process of decomposition of supersaturated solid solution of the CuNi16Al5 alloy during its ageing at the temperature of 550^0C commences with formation of the coherent spherical precipitates. As the process proceeds, these precipitates grow and undergo morphological changes according to the scheme:

nucleation and growth of spherical precipitates $\rightarrow$ formation of a sub-structure of spherical precipitates and acquiring a specific orientation by them $\rightarrow$ the shape change of the precipitates from spherical to cubic and taking privileged positions along the <100> direction of a matrix

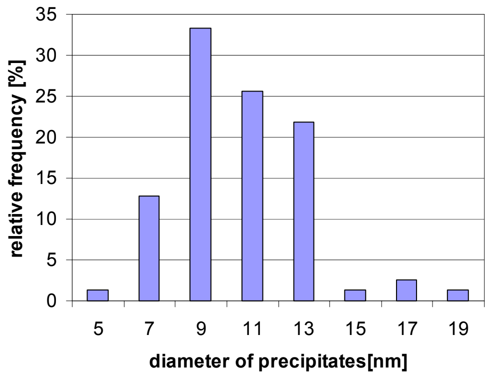
The spherical shape of the precipitates remains stable up to about 48 hours of ageing. At higher ageing times, an average precipitate volume is about $2x10^4$ nm^3. As the ageing time increases, the greatest precipitates continue to grow and change their shape to cubic, whereas the remaining ones diminish slowly and gradually until they decay completely. On the histograms it manifests itself by the formation of two frequency maxima (Figs 3f, 4b,d,f). With the ageing time increase they shift towards lower values of volume in the case of spherical precipitates or higher values – in the case of cubic precipitates. It should be emphasised that the spectrum corresponding to cubic precipitates initially widens (standard deviation increases), and only at very high ageing times the standard deviation stabilises at a lower level, which proves uniformity of the size of the precipitates. It is worth noting that the changes in average values of a volume of particular precipitates with the increase of ageing time are not monotonous, which refers both to spherical and cubic precipitates. Besides, a clear interaction between the precipitates becomes apparent. The change of a curve illustrating changes in an average precipitate volume with ageing time indicates that interaction between precipitates is of an attractive character.

The investigation carried out under this work fully confirmed a competitive effect of an elastic strain energy, surface energy on the matrix-precipitate inter-phase boundary and the energy of elastic interaction between precipitates on the morphology of coherent precipitates [1, 13-16]. Precipitates of the Ni_3Al phase in a copper matrix nucleate and grow as spherical precipitates, which evidences that the process is controlled by a surface energy. The influence of elastic strain energy and the interaction energy on the shape of Ni_3Al phase precipitates becomes visible in the further stages of the alloy ageing process, with the increase of the volume of precipitates and the change of a distance between them. At that time, the spherical precipitates undergo transformation into cubic ones. The driving force for precipitate shape changes is a reduction in elastic strain energy caused by elastic interaction of precipitates which orient the cubes to the elastically soft matrix directions <100>. This strain energy reduction, estimated for 35 nm spherical Ni_3Al is about 1 MJ/m^3. It compensates the increase of the surface energy of precipitates, resulting from an increase of precipitates surfaces during transformation from sphere to cube.

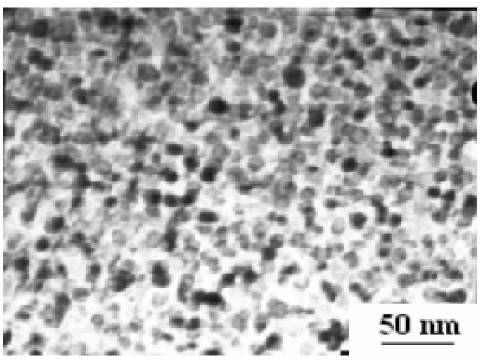
a)



b)



c)



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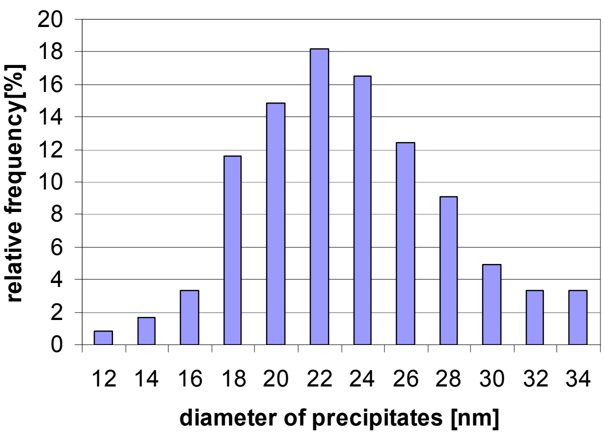
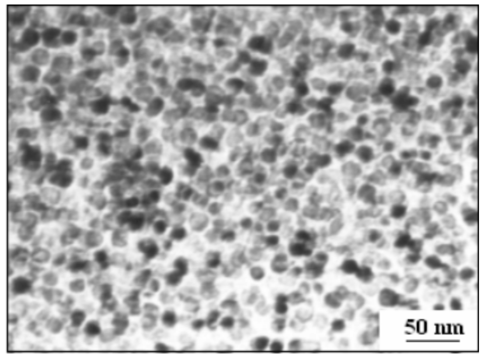


e)



f)

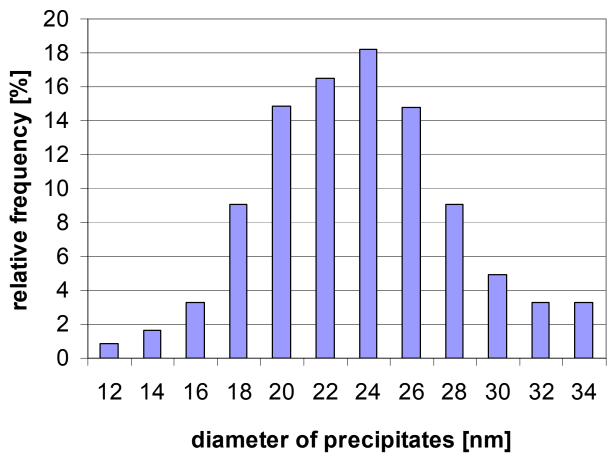


Fig. 1. Exemplary microstructures and precipitate size distributions of the CuNi15Al5 alloy aged at 450°C for 24 (a, b), 96 (c, d), and 380 hours (g, h), d – electron diffraction pattern from selected areas as in Figs.1a, representative for all microstructures

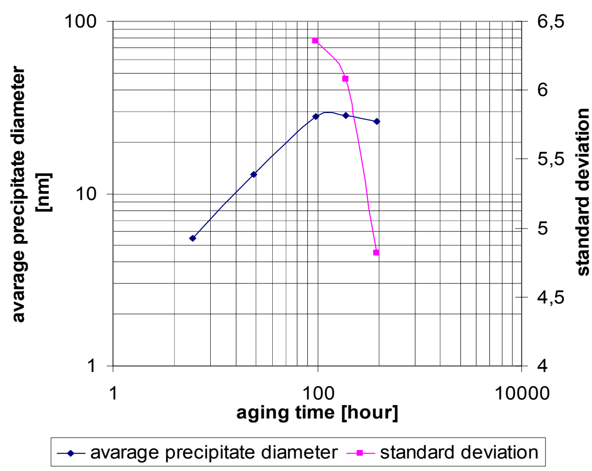
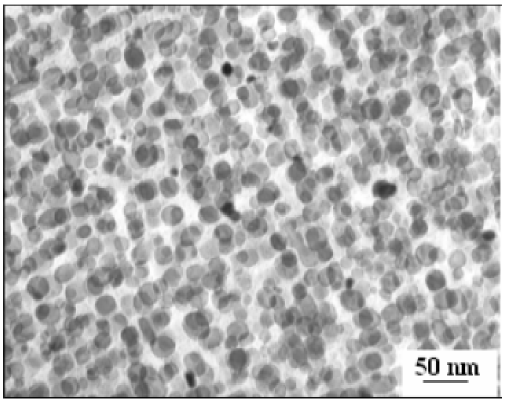
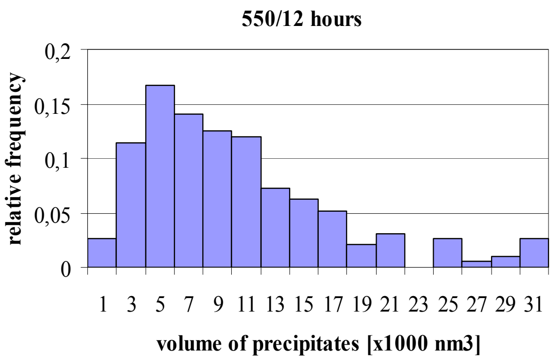


Fig. 2. The changes of an average precipitate diameter for the Ni_3Al phase and standard deviation of precipitates size distribution for the CuNi16Al5 alloy in dependence on ageing time

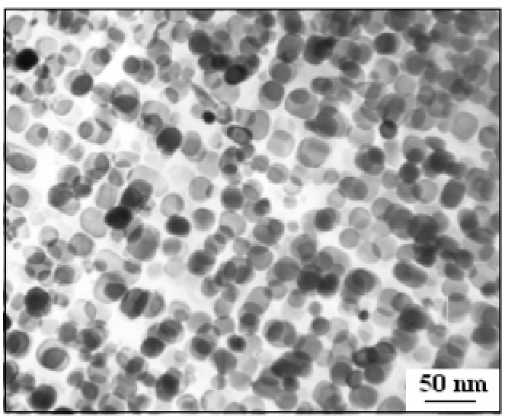
a)



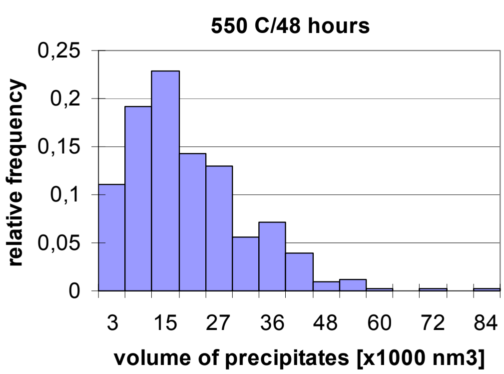
b)



c)



d)



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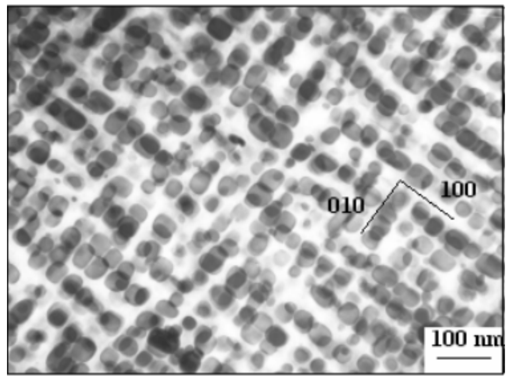

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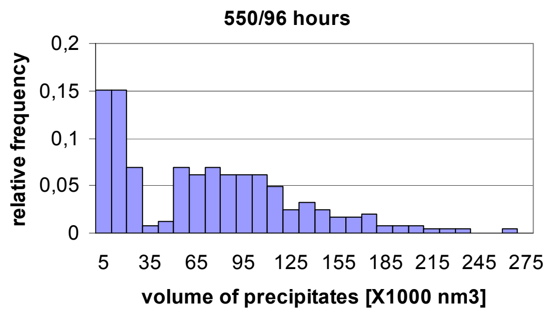
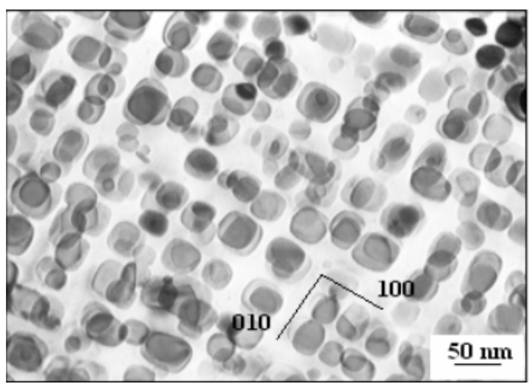
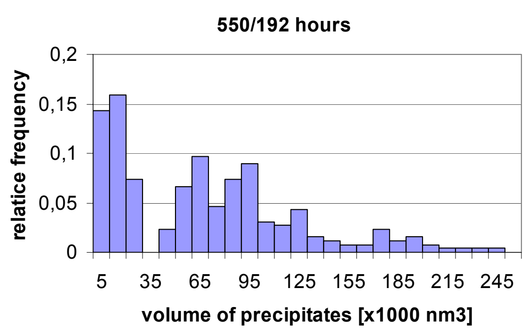


Fig. 3. TEM images of a microstructure and precipitates size distributions of the CuNi15Al5 alloy aged at 550 ^{o}C for 12 (a, b), 48 (c,d) and 96 (e, f) hours

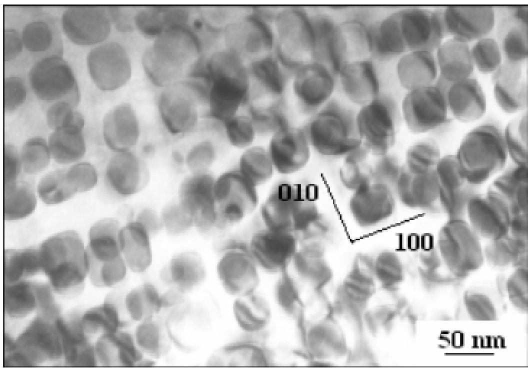
a)



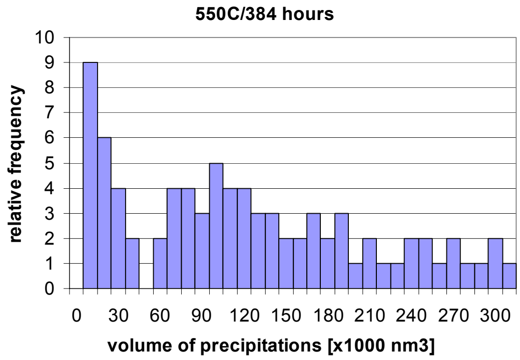
b)



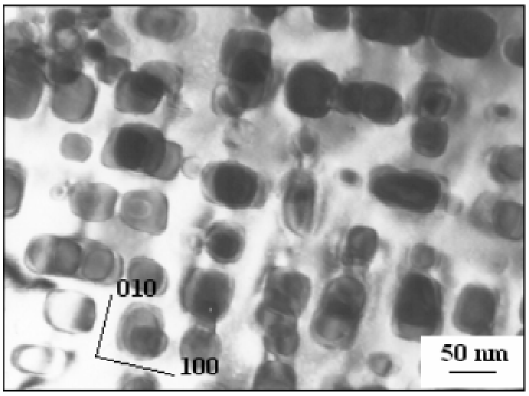
c)



d)



e)



f)

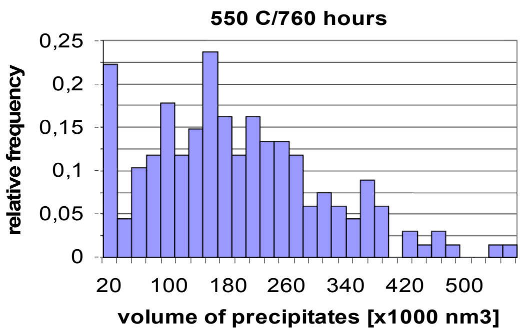


Fig. 4. TEM images of a microstructure and precipitate size distributions of the CuNi16Al5 alloy aged at 550 °C for a 192 (a, b), 384 (c, d) and 760 (e, f) hours

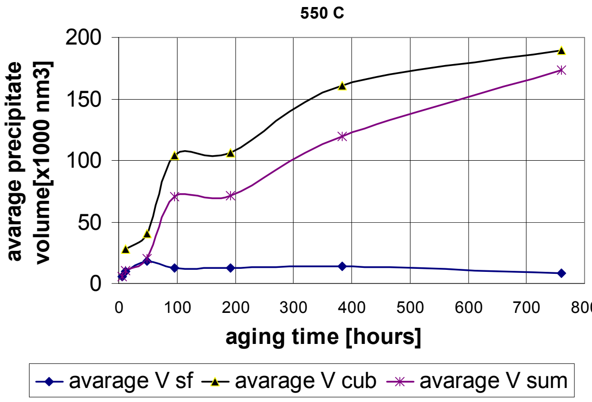


Fig. 5 Change of an average volume of the Ni_3Al phase precipitates with ageing time in the CuNi16Al5 alloy aged at 550 °C

The results obtained from this investigation indicate wide possibilities of the precipitate morphology changes by the changes of a self-energy of elastic strain of particular precipitates and of an energy of interaction between them. The high elastic strain energy on the matrix-precipitate inter-phase boundary slows down the process of precipitates coagulation in the copper alloys. In the alloys with significant volumetric fraction of the precipitates and at high degree of their dispersion it is possible to obtain almost the same size of precipitates within a wide range of ageing times. This effect can be practically used to stabilise properties of precipitation-hardened copper alloys designed for application at elevated temperatures.

4. Conclusions

The precipitation mechanism taking place in the CuNi16Ni5 alloy aged at the temperatures of 450 and 550°C for up to 760 hours was investigated. The results obtained justify formulation of the following conclusions:

- Within the investigated temperature range and ageing time, the decomposition process in supersaturated solid solution proceeds by nucleation and growth of the coherent precipitates of the $L1_2$ – Ni_3Al phase,
- Morphology of these coherent precipitates changes as a result of competitive influence of an elastic strain energy, surface energy on the matrix-precipitate inter-phase boundary, and the energy of elastic interaction between precipitates. The $L1_2$ –Ni_3Al precipitates nucleate as the spherical ones and grow, forming intermediate sub-structures, until they reach a cubic form with the planes parallel to the{100} planes of a matrix and take privileged positions along the <110> directions.
- Coagulation of the Ni_3Al phase precipitates from super-saturated solid solution of copper proceeds similarly as in nickel super-alloys of high elastic strain self-energy of the precipitates and high energy of interaction between them. Clear deviations from the LSW coagulation theory and its modifications, demonstrated by the slow-down of the process, have been observed. In an extreme case, growth of the precipitates can be completely stopped in some time ranges of the ageing process. This effect can be used in practice to stabilise mechanical properties at elevated temperature.

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