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Precipitation Effects in Cu-Ni-Sn and Cu-Ti Alloys

O. DRÁBOVÁ, P. VOSTRÝ, F. PEŠEK, B. SMOLA*)

Czechoslovakia

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The decomposition of the supersaturated solid solutions of Cu-Ni-Sn and Cu-Ti and the influence of the prestrain on this process were investigated by means of electrical resistivity and yield stress measurements completed by TEM, ED, X-ray and light microscopy analyses. Specimens of Cu-9.8at.% Ni-4.2at.%Sn and Cu-2.5at.%Ti alloys homogenised for 4 hours at 1163 K and 1023 K, respectively were isochronally annealed in the temperature range 373—1173 K and 323—1173 K, respectively.

The development of the coherent metastable phase γ' followed by the nucleation of the incoherent equilibrium phase γ was found in the temperature range 570—770 K in Cu-Ni-Sn alloy. These precipitation effects are preceded by the spinodal decomposition. The dissolution of the developed structure accompanied by the primary recrystallization starts at 800 K. Great particles of a new cubic phase were observed between 850—900 K.

The spinodal decomposition in the Cu-Ti is followed by the development of the metastable phase β'. Then incoherent particles of the stable phase β appear. Both phases dissolute at temperatures above 900 K. An unknown phase was seen in the material at all annealing temperatures. We suppose this phase to be responsible for the complexity of the resistivity changes observed above 900 K. The primary recrystallization begins at about 1000 K.

Introduction

Recently the pre-precipitation and precipitation processes in Cu-Ni-Sn and Cu-Ti supersaturated solid solutions were studied especially owing to their effect on mechanical properties of these alloys [1—8], which can be used commercially. This investigation was undertaken mainly by means of the isothermal annealing at selected temperatures.

We studied the decomposition of the supersaturated solid solutions of Cu-Ni-Sn and Cu-Ti alloys by means of the isochronal annealing in the wide range of temperatures starting at the room temperature. In our earlier paper [9] we reported the results of the experiments performed below 573 K with the use of electrical resistivity, microhardness and lattice parameter measurements. The influence of the prestrain was

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*) Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 121 16 Praha 2, Czechoslovakia.

also studied. Two stages were observed on the resistivity annealing curves of both alloys: the nature of the stage situated at lower temperatures is not yet known, the second one was found to be due to the onset of the spinodal decomposition of the supersaturated solid solution. The first stage is not influenced by the prestrain, while the second one is strongly suppressed due to the prestrain. This fact was explained by the solute-dislocation interaction resulting in the clustering of solutes at dislocations, which leads to the suppression of the spinodal decomposition.

It is the aim of this paper to report the results of the investigation of pronounced microstructure changes in the wider temperature range up to 1173 K. This investigation was performed by means of electrical resistivity and yield stress measurements. We used the isochronal annealing procedure again but with a longer annealing step. Electrical measurements and mechanical tests were accompanied by TEM, ED, X-ray and light microscopy observations.

Experimental details

The specimens of Cu-9.8at.%Ni-4.2at.%Sn and Cu-2.5at.%Ti had the form of the ribbons of 0.1 mm and 0.2 mm in thickness, respectively. At first they were exposed to the homogenisation annealing for 4 hours at 1163 K and 1023 K, respectively. A part of them was prestrained in tension at room temperature with the strain rate of $1.25 \, . \, 10^{-4} \, s^{-1}$ to the strains 5, 10 and 15 %. Then the specimens were isochronally annealed in the temperature range 373 − 1173 K (Cu-Ni-Sn) or 323 − 1173 K (Cu-Ti) in a stepped program 50 K/1 hour. Both homogenisation and isochronal annealing were carried out in argon atmosphere and finished by water quenching. Electrical resistivity was measured in liquid nitrogen by means of the dc four points method with an accuracy of 0.01 %. Tensile tests were performed in tension at room temperature with the rate of $2.65 \, . \, 10^{-4} \, s^{-1}$. Optical metallography, TEM, ED and X-ray analysis were carried out at room temperature, X-ray analysis by the Debye-Scherrer's method.

Experimental results and discussions

1. Cu-Ni-Sn

Differential electrical resistivity annealing curves are plotted in Fig. 1. The shape of these curves can be explained with the use of TEM and ED analysis published recently in [10]. The acceleration of the resistivity decrease between 550 K and 770 K is due to the formation of fine coherent particles of the metastable γ' phase of the DO_{22} structure. Above 600 K the lamellar structure of the stable γ phase with the DO_3 structure begins to appear. Both phases have the chemical composition of $(Cu_xNi_{1-x})_3Sn$. The appearance of incoherent γ phase particles and their growth result in the slower resistivity decrease above 600 K, where both phases coexist.

Another local maximum is seen at 750 K (Fig. 1). This effect is connected with the repeated formation of γ' particles. which is in the agreement with a complex form of PTT diagram of this alloy [11].

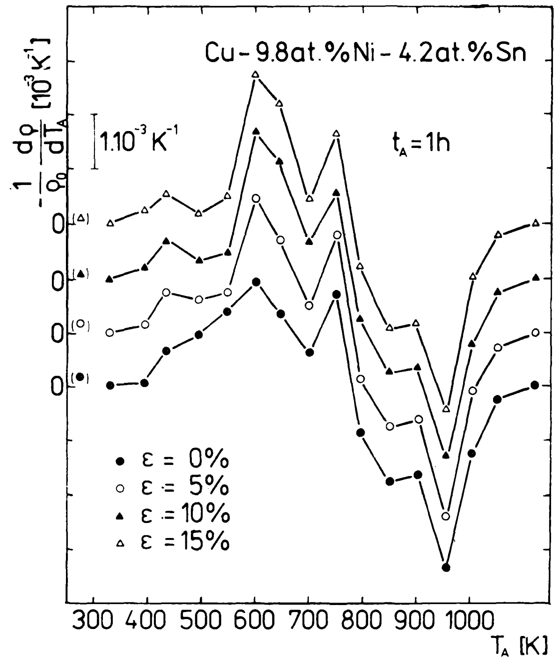

Fig. 1. Temperature derivatives of electrical resistivity annealing curves of Cu-9.8at.%Ni-4.2at.%Sn alloy ϱ_0 is a value of ϱ in the as-quenched state

The redissolution of the particles of both phases starts at 770 K with the resistivity increase as a result. The lowering of the rate of the resistivity increase between 850—900 K is due to the transformation of the lamellar γ phase particles into great particles of a new phase at grain boundaries moving during the recrystallization. The composition of this new phase was found to be about 70at.%Ni, 8at.% Sn and the Cu balanced [10]. Its crystal structure can be described by the unit cell of fcc lattice with the lattice parameter (1.07 ± 0.02) nm [10]. The increase of annealing temperature above 900 K leads to the dissolution of this cubic phase into the matrix with the stable solid α-solution as the result.

As it was proved by light microscopy and X-ray analysis the primary recrystalization starts at about 820 K. It follows from the optical metallography that the growing of recrystallized grains occurs by the mechanism of Bailey. The decay of Debye-Scherrer's lines into the individual spots is complete at 1073 K and the primary recrystallization finishes. Resistivity changes measured above 800 K are not influenced by the value of the prestrain. Thus these changes are due to the redistribution of solutes mainly and the contribution of the primary recrystallization is hidden.

The influence of the phase transformation on mechanical properties was also studied. Isochronal annealing curves of yield stress are shown in Fig. 2. Their shape corresponds well with the resistivity measurements. It is obvious that the appearing of DO_{22} coherent particles is connected with the increase of yield stress, while its decrease is always due to the formation of the stable lamellar DO_3 precipitates. These results are in accordance with [10, 11].

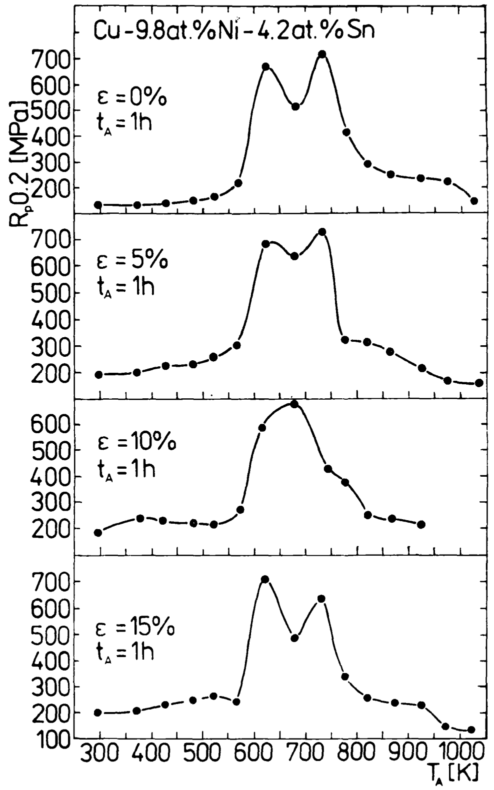

Fig. 2. Yield stress annealing curves of Cu-9.8at.%Ni-4.2at.%Sn alloy

2. Cu-Ti

Differential resistivity annealing curves of Cu-Ti for various values of the prestrain are seen in fig. 3. The local maximum at 500 K, which is suppressed by the prestrain is caused by the spinodal decomposition of the supersaturated solid solution [9]. The presence of the modulated structure and side-bands was confirmed by TEM and ED observations. Great spherical particles of an unknown phase were seen in specimens at all annealing temperatures. They originated probably during the melting of the alloy and did not dissolute by the homogenisation annealing. This phase contains Ti and Cu in the ratio of about 1 : 3 according to EDX analysis and it is probably a high-temperature modification of the equilibrium phase β or some of Cu-Ti oxides.

The rate of the resistivity decrease reaches the absolute maximum at 650 K.

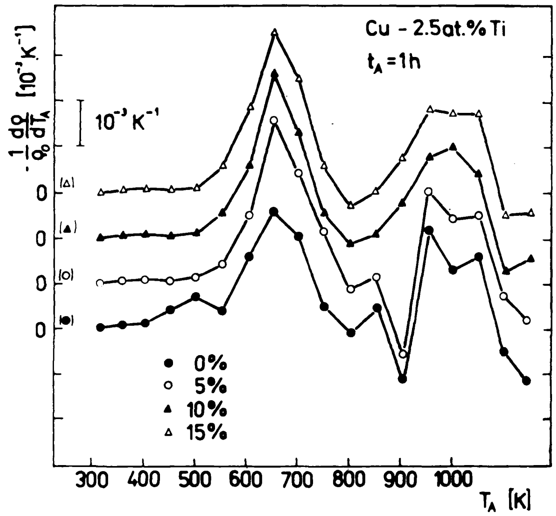

Fig. 3. Temperature derivatives of electrical resistivity annealing curves of Cu-2.5at.%Ti alloy ϱ_0 is a value of ϱ in the as-quenched state

The modulated structure disappears and is replaced by small coherent particles probably of the metastable phase β' with the composition of Cu_4Ti [12]. Some incoherent particles were also observed, their formation leads to the lowering of the rate of resistivity decrease above 650 K. The resistivity stays almost constant in the temperature range 750–850 K. TEM and ED confirmed the coexistence of two types of phases at 873 K: the developed system of coherent precipitates β' and incoherent lamellar particles of the stable phase β. The phase β with the composition of Cu_3Ti has an orthorombic lattice with the parameters near to $a = 0.517$ nm, $b = 0.435$ nm, $c = 0.453$ nm published in [13].

The nature of the resistivity increase at 900 K and its suppression by the prestrain is not yet clear.

Both the metastable phase β' as well as the incoherent particles of phase β dissolute at temperatures above 900 K. Only spherical particles of unknown phase are present in the matrix at 1073 K. Resistivity decreases strongly in this temperature range again. It is in the contradiction to the behaviour of Cu-Ni-Sn alloy, where the return of the alloy to the simple state of solid solution was observed with the resistivity increase to its initial value as the result. We ascribe tentatively this effect to the absorption of Ti atoms by the spherical particles after the dissolution of β and β' phases particles.

Accordingly to the X-ray analysis the primary recrystallization begins at about

973 K, when individual spots appear on the Debye-Scherrer's lines. The material is completely recrystallized at 1073 K.

Conclusion

The decomposition of the supersaturated solid solutions of Cu-Ni-Sn and Cu-Ti and the influence of the prestrain on this process were investigated.

The coherent metastable phase γ' develops in Cu-Ni-Sn followed by the formation of the lamellar incoherent equilibrium phase γ in the temperature range 570–770 K. These precipitation effects are preceded by the spinodal decomposition. The dissolution of the developed structure accompanied by the primary recrystallization starts at 800 K. Great particles of the new cubic phase were also observed between 850–900 K. They dissolute into the matrix above 900 K. The primary recrystallization finishes at about 1070 K.

The spinodal decomposition in Cu-Ti is followed by the development of the metastable phase β' and by the appearance of incoherent particles of the stable phase β in the temperature range 550–850 K. Both phases dissolute at temperatures above 900 K. Spherical particles of an unknown phase observed in the material at all annealing temperatures are probably responsible for the complexity of effects observed on the resistivity annealing curves above 900 K. The primary recrystallization takes place between 970–1070 K.

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