

DECOMPOSITION OF THE SUPERSATURATED SOLID SOLUTION IN THE Cu-Ni-Sn SYSTEM

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Received 18 October 1983

Revised manuscript received 15 December 1983

UDC 538.91

Original scientific paper

The strengthening of the Cu-10 wt. % Ni-4 wt. % Sn supersaturated solid solution during ageing was followed by hardness measurement. The corresponding changes in structure were followed by optical microscopy and x-ray diffraction. After initial fast increase in hardness caused by spinodal decomposition a maximum in hardness is reached that corresponds to a decomposition of the matrix into two f.c.c. structures with different lattice parameters. The decrease in hardness after longer ageing times is caused by discontinuous precipitation of equilibrium $\alpha + \gamma$ phase and recrystallisation of the matrix.

1. Introduction

The structural changes taking place during the decomposition of the copper rich Cu-Ni-Sn supersaturated solid solution have been examined by x-ray diffraction and transmission electron microscopy by many authors¹⁻⁴. It was established that at concentrations of 8—15 wt. % Sn the alpha solid solution decomposes in two different ways, depending on temperature. At 450°C and lower temperatures spinodal decomposition takes place, whereas at temperatures above 450°C a coherent phase nucleates at the grain boundaries and in deformed regions of the matrix.

This phase grows in the form of Widmanstätten plates. By electron diffraction it was found that the tin-rich product of the spinodal decomposition and the Widmanstätten plates have the same ordered tetragonal DO_{22} structure⁴⁾.

After longer ageing even at temperatures below 450 °C Widmanstätten precipitates form at grain boundaries. As the final step in the decomposition, after longer ageing times, the matrix undergoes a discontinuous cellular transformation into the equilibrium $\alpha + \gamma$ mixture. The gamma phase has the DO_3 , i. e. ordered $L1_2$ (Cu, Ni)₃Sn structure.

The investigation of mechanical properties showed that the spinodal decomposition considerably increases the hardness in this system. The grain boundary precipitates cause embrittlement, whereas the appearance of the $\alpha + \gamma$ equilibrium structure is accompanied by a fast drop in strength^{2, 3, 5)}.

Since the described structural changes have specific effect on the mechanical properties of this alloy, a broad study was initiated in order to establish the conditions which enable the achieving of the optimal ratio between strength and ductility, and the corresponding structure/property relations. In the present paper the change in hardness of the supersaturated solid solution of the Cu-10 wt. % Ni-5 wt. % Sn alloy was followed during ageing in the temperature range from 300 to 450°C. The hardness was correlated with structural changes as revealed by x-ray diffraction and optical microscopy.

2. Experimental

The alloy was produced in a laboratory furnace by induction melting of technically pure components. Chemical analysis furnished the following composition of the alloy: 10.0 wt. % Ni and 4.8 wt. % Sn. Chill cast ingots were homogenized at 800°C and cold rolled into 1 mm thick strips. The final heat treatment consisted of solution annealing for 1 hour at 825°C, followed by water quenching and ageing for various times (from 1 min to 24 hours) in the temperature range from 300 to 450°C in a salt bath.

Aged samples were polished and then etched in a sulphuric acid-hydrogen peroxide mixture. Microstructure was examined by optical microscopy. The Vickers hardness of these samples was measured.

X-ray diffraction analysis was performed on a diffractometer with filtered $CuK\alpha$ radiation.

3. Results

X-ray diffraction

Solution annealed and quenched samples had the f.c.c. structure of the supersaturated solid solution. The lattice parameter $a = 0.3629$ nm is higher than that of pure copper ($a = 0.36141$ nm).

The lattice parameter of the f.c.c. solid solution decreases with ageing time. At 300°C this change is small and linear up to more than 24 hours (Fig. 1). At 350°C the lattice parameter has a similar trend up to 16 hours and then a steeper drop sets in. At 400°C the lattice parameter has fast decrease even at the earlier

stages of ageing. The final value of the lattice parameter ($a = 0.3611$ nm) becomes even lower than that of pure copper.

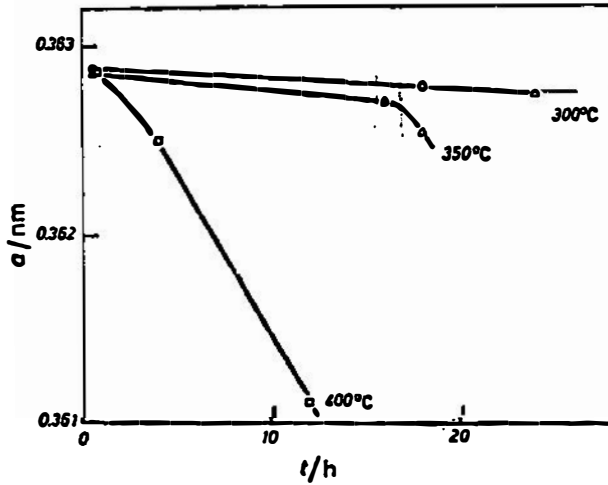


Fig. 1. Change of lattice parameter with ageing time.

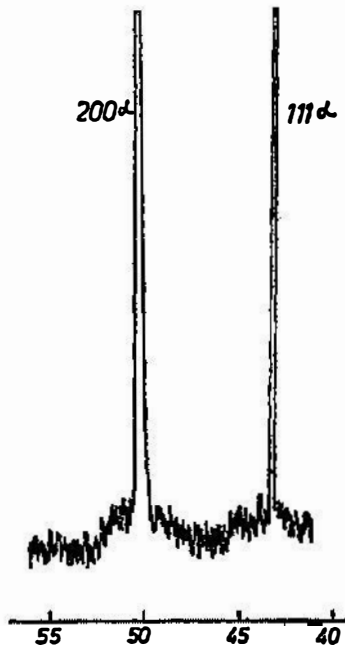


Fig. 2. Sideband reflections around fundamental x-ray lines in the sample aged 1 hour at 350°C

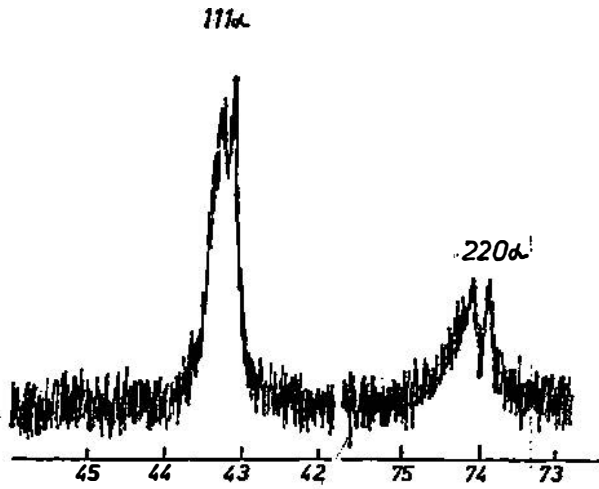


Fig. 3. The split x-ray lines in sample aged 18 hours at 350°C.

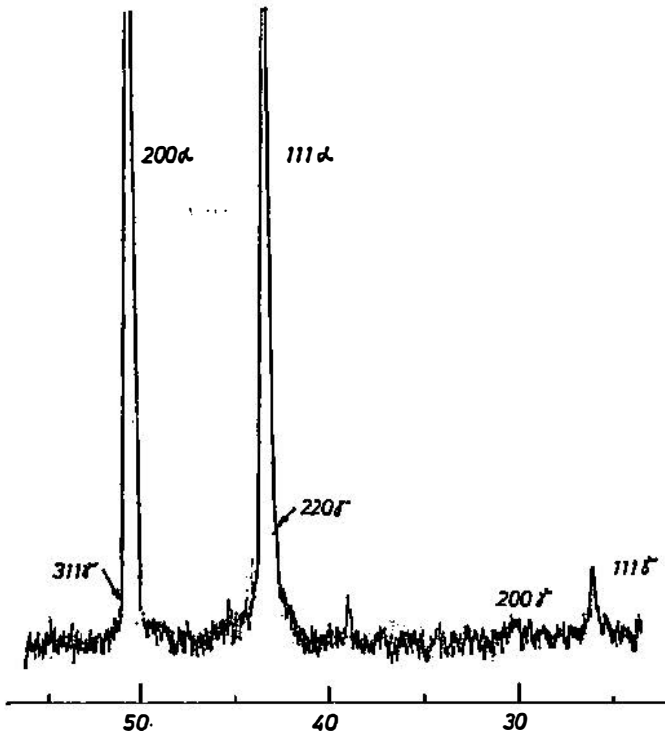


Fig. 4. X-ray lines of the $(\text{Cu, Ni})_3\text{Sn}$ phase (γ) beside the fundamental f.c.c. lines. Sample aged 12 hours at 350°C.

In addition to the decrease in lattice parameter, some changes in the shape of the x-ray reflections take place during ageing. In the first instant this is the appearance of asymmetrical sideband reflections in the vicinity of fundamental x-ray reflections (Fig. 2). Further ageing leads to the broadening of the x-ray reflections, and then the reflections split into two lines of similar intensity (Fig. 3).

After longest ageing times marked x-ray lines of the equilibrium $(\text{Cu}, \text{Ni})_3\text{Sn}$ phase appear (Fig. 4). The matrix diffraction lines become sharp again.

Optical microscopy

The microstructure of the quenched samples consists of polygonal grains of the solid solution, with regular grain boundaries (Fig. 5). The first change that can be detected by optical microscopy is the precipitation of fine particles at the

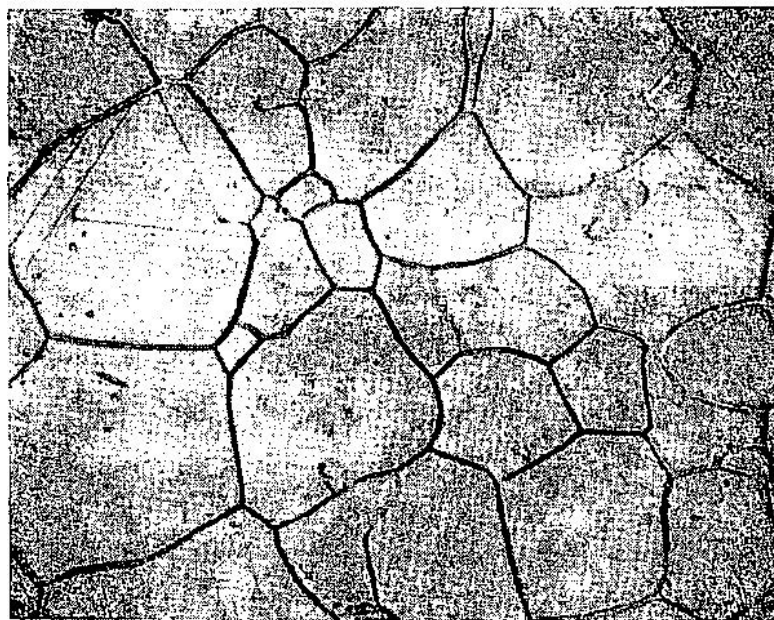


Fig. 5. Microstructure of the quenched alloy, x425.

grain boundaries after high temperature ageing (Fig. 6). At longer ageing times a lamellar product develops at grain boundaries and in the matrix as the result of discontinuous cellular transformation (Fig. 7).

Hardness measurement

Structural changes that take place during the decomposition of the super-saturated solid solution are accompanied by the changes of mechanical properties.

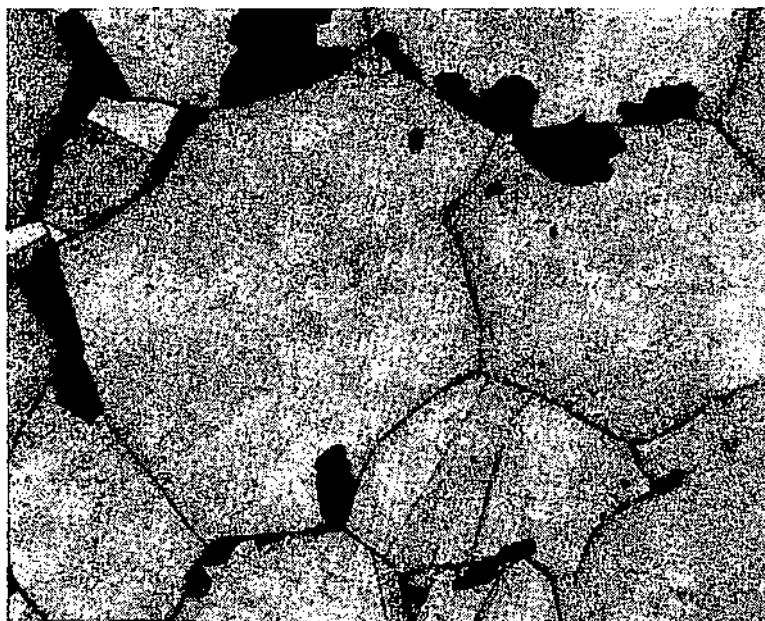


Fig. 6. Grain boundary precipitates in the sample aged 16 hours at 350°C, x425.



Fig. 7. Discontinuous cellular transformation in sample aged 12 hours at 450°C, x1800.

Fig. 8 shows the effect of ageing on hardness. It is evident that ageing in the temperature range 300–450°C, after shorter incubation period leads to substantial hardening. The hardness curves reach a maximum, and after longer ageing times the hardness drops. The length of the incubation period apparently follows a C type kinetics, which was more thoroughly examined in another paper⁵⁾. The maximal hardness is achieved at lower temperatures, and it decreases with raising temperature.

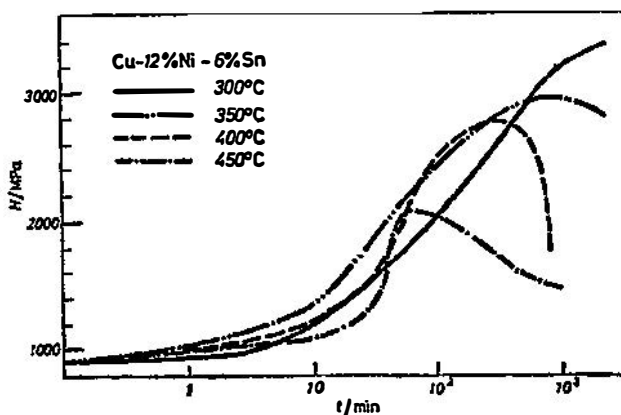


Fig. 8. The effect of ageing temperature on hardness.

4. Discussion

Parallel investigation of structural changes and mechanical properties gives a broader insight in the decomposition of the supersaturated solid solution of the Cu-Ni-Sn system.

The quenched solid solution has a larger lattice parameter than pure copper, because of large lattice dilatations caused by solution of tin. Solution of nickel decreases the copper lattice parameter. In both cases the changes are linear⁶⁾. The lattice parameter of the ternary Cu-Ni-Sn alloy shows also a certain linearity with alloy composition. Namely, starting with a binary copper alloy, the addition of the third element changes the lattice parameter following a linear relationship that has the same slope as it would have if this element was added to pure copper. This construction was verified by plotting the experimental results of lattice parameter and chemical compositions obtained by other authors. It enables the estimation of the change in composition that takes place during the decomposition of the Cu-Ni-Sn solid solution. The early stages of decomposition of the supersaturated solid solution are characterized by spinodal decomposition. In previous investigations^{3,4)} this reaction was thoroughly studied. The changes in size and shape of the x-ray line sidebands have been correlated with the modulation of chemical composition on microscale and the size of the microregions. Therefore, there was no need to enter such an analysis in the present work, particularly because the experimental equipment, without a monochromator, was not appropriate for this type of work.

The present study shows that in addition to the appearance of sidebands certain changes in the position and shape of the fundamental x-ray reflections of the matrix take place during decomposition of the solid solution.

The decrease of lattice parameter observed during ageing is caused by removal of tin from the solid solution. The change is in the beginning linear and corresponds to the spinodal reaction. Later, the drop in lattice parameter becomes steeper, probably due to more abundant coherent precipitation and discontinuous precipitation. This correlates well with the hardness measurements discussed below.

The solid solution is harder than pure copper due to the presence of solute atoms of different size. They produce localized elastic strain fields which interact with those of dislocations, making the movement of dislocation more difficult. The spinodal decomposition is accompanied by a relatively steep increase in hardness. The formation of coherent spinodal clusters introduces additional elastic stresses into the matrix which efficiently oppose dislocation movement, i. e. plastic deformation. However, the maxima in the hardness curves correspond to such changes in the structure that modify the fundamental x-ray reflections of the matrix phase. It can be assumed that the observed broadening and splitting of the f.c.c. peaks correspond to the state when the basic structure, due to the modulation of chemical composition on microscale practically decomposes into two separate f.c.c. lattices of defined compositions and lattice parameters. Measurement of Bragg angles that correspond to the split peaks reveal a difference of 1.5 to 2 wt. % in tin content between these lattices, under assumption that diffusion of tin atoms causes the modulation in composition. The existence of two lattices with different parameters introduces high straining of the structure that hinders the movement of gliding dislocations and accordingly strengthens the alloy.

Microscopic investigations show that in the moment when the hardness reaches maximum value the matrix starts to transform by discontinuous precipitation of very fine lamellae of $\alpha + \gamma$ phase. This transformation is probably favoured by separation of components which starts by spinodal decomposition and proceeds by formation of two structures of different composition. More intensive development of $\alpha + \gamma$ phases sharply decreases the hardness. This is understandable because the transformation furnishes equilibrium products, removes the majority of internal stresses by recrystallization of the matrix, and thus lowers the strength of the alloy. At this time the lattice parameter of the f.c.c. structure falls below the value for pure copper, which means that the matrix is depleted of tin and consists primarily of Cu-Ni solid solution.

The observation that at lower temperatures of the investigated region higher hardness levels are achieved could be explained by the fact that the rate of diffusional processes increases with raising temperature and so the discontinuous transformation starts earlier, causing the drop in hardness at higher temperature.

5. Conclusions

The increase in hardness of the aged alloy is a result of spinodal decomposition of the supersaturated solid solution. The presented x-ray diffraction results show that the maximal hardness corresponds to a state in which the spinodal struc-

ture becomes stable and consists of regions rich on tin and regions depleted of tin, each with a defined lattice parameter.

The discontinuous precipitation of equilibrium $(\text{Cu, Ni})_3\text{Sn}$ phase, after longer ageing times, causes fast decrease in hardness.

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RAZLAGANJE PRESIĆENOG ČVRSTOG RASTVORA U SISTEMU Cu-Ni-Sn

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UDK 538.91

Originalni naučni rad

Ojačavanje presićenog čvrstog rastvora legure Cu-10 tež. % Ni-4.8 tež. % Sn pri starenju praćeno je merenjem tvrdoće. Odgovarajuće promene strukture praćene su optičkom mikroskopijom i rendgenskom difrakcijom. Posle početnog brzog povećanja tvrdoće, izazvanog spinodalnim razlaganjem, dostiže se maksimum tvrdoće koji odgovara razlaganju osnove na dve površinski centrirane kubne strukture sa različitim parametrima rešetke. Pad tvrdoće posle dužih vremena starenja izazvan je diskontinuiranim taloženjem ravnotežne $\alpha + \gamma$ faze i rekristalizacijom osnove.