THE EFFECT OF COLD DEFORMATION ON THE KINETICS OF THE SPINODAL DECOMPOSITION OF Cu−9Ni−6Sn−0.3Ce ALLOY①

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ABSTRACT

By means of the measurement of mechnical properties and resistivity and X−ray diffraction and transmission microscopy, the effect of cold deformation on the kinetics of spinodal decomposition of Cu−9Ni−6Sn−0.3Ce alloy was studied. The strengthening process of the cold-worked and aged alloy was found to be accelerated. Using the theory of dislocation, the strengthening in cold-worked alloy can be attributed to the acceleration of spinodal process.

Key words: Cu−9Ni−6Sn−0.3Ce, Spinodal decomposition, cold-worked alloy.

1 INTRODUCTION

The Cu−Ni−Sn alloy is the typical alloy which undergoes spinodal decomposition. It has been found that the strength of cold-worked and aged alloy was higher than that of annealed and aged alloy. The former alloy reached the peak strength value much faster. Concerning this phenomenon, Plewes[1] believed that the cold deformation altered the kinetics of spinodal decomposition, increased the amplitude of the modulation decomposition. But Spooner and Lefever[2] argued that it could not be attributed to the change of spinodal decomposition or coarsening kinetics, but it was the dislocation caused by cold deformatiom that made DO_{22} matrix interfaces have a lower total elastic strain energy. The observed strengthening is the interaction between the modulated spinodal and the dislocation substructures. In order to clear the essence of the effect of the cold deformation on the strengthening, the effect of cold deformation on the kinetics of spinodal decomposition and on the strengthening has been studied.

2 EXPERIMENT

The alloy was melted in a vacuum alumina crucible under Ar atmosphere, and was cast and homogenized at 820 ℃ for 6 h, then quenched in water . The alloy was cold rolled and drawn into wire of 0.19 mm in diameter and plate of 0.05 m in thickness at room temperature.

The wire samples were first annealed in charcoal at 820 ℃ for 2 h and quenched in

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water. Then the samples were further aged at 350 ℃ for different times. The strength was measured by FM3 pulling test and the resistivity was measured by QJ19 electrical bridge at room temperature.

The plate samples with 92% deformation, annealed at 820 ℃ for 2 h and quenched in ice water were further aged at 350 ℃. The side-band on (200) diffraction was analysed using D / max-rc diffractometer and CuK_α at 50 kV.

The microstructures of these samples were observed with JEM-2000EX transmission electron microscopy.

3 RESULTS

3.1 *The Effect of Cold deformation on the Mechanical Property and Resistivity*

The relation of strength and ageing time is shown in Fig.1, from which we found the strength of quenched samples reached the maximum in about 16 h, but for cold-worked sample the maximum strength value can be reached in 10 min. Further more, the latter one is about 30% higher than that of the former, but it drops quickly after ageing for 100 min and the alloy becomes brittle. A typical ρ vs t plot is shown in Fig2, from which we found the resistivity of the cold-worked and aged samples dropped faster than that of the annealed and aged samples. The following equations were obtained from the regular equation group:

for annealed & aged alloy

$$\rho = \rho_0 \exp(-0.002,542\, t) \quad (1)$$

for cold-worked & aged alloy

$$\rho = \rho_0 \exp(-0.009,99\, t) \quad (2)$$

where ρ_0—resistivity of the quenched sample, $\mu\Omega$cm;

t—ageing time, min

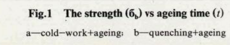


Fig.1 The strength (σ_b) vs ageing time (t)

a—cold-work+ageing; b—quenching+ageing

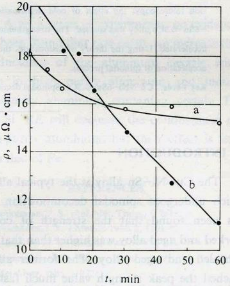


Fig.2 Resistivity (ρ) vs ageing time (t)

a—cold-work+ageing; b—annealling+ageing

3.2 *The Effect of Cold Deformation on the Modulation Wavelength*

The effect of cold deformation on the modulation wavelength of the alloy was studied by means of sidebands analysis of X-ray diffraction. We find the sideband intensities of the aged sample are different even if the two samples were aged at the same temperature and for the same time. The modulation wavelength may be developed from the Daniel-Lipson formula[3]

$$\lambda = ha_0 \tan\theta / (\triangle\theta)(h^2+k^2+l^2) \quad (3)$$

where θ—the Bragg diffraction angle for the (hkl) reflection;

$\triangle\theta$—the angular displacement of the sideband from (hkl) line of Bragg angle (θ);

a_0 —the lattice constant, for the (200) reflection h=2

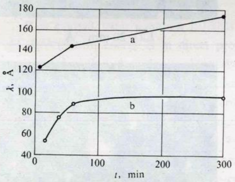


Fig.3 The modulation wavelength (λ) vs ageing time (t)

a—cold-work+ageing; b—anneeling+ageing

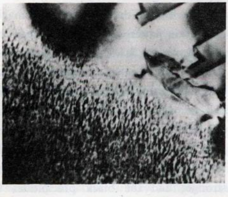
The relation of modulation wavelength and ageing time is shown in Fig.3, from which we found the modulation wavelength of cold-worked and aged sample is larger than that of the annealed and aged one.

3.3 *TEM observation*

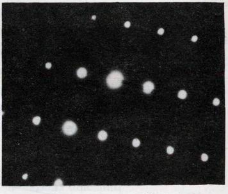
We have found through the TEM observation of Cu−9Ni−6Sn−0.3Ce alloy that the string contrast appeared in the sample quenched and aged for 10 min and the string contrast increased with ageing time. The precipitates appeared at grain boundaries. The diffraction pattern of the second phase were found by the electron diffraction. A large string zone can be observed in the cold-worked samples aged for 10 min and black precipitates appear, if aged for 60 min. Fig.4 shows the comparision of the bright fields image and diffraction patterns of the alloy aged for 300 min. From Fig.4 we can see the modulation structure in annealed and aged alloy becomes coarsing, large precipitates appear within grain and the diffraction pattern of second phase can be observed. From the bright field image, it can be seen that the recrystallization already took place the diffraction pattern became stronger and the black precipitates within grains more obvious.

4 DISCUSSION

The differences of mechanical and electrical properties of two aged alloys indicate the different kinetics of their structure changes, which have been confirmed by sideband analysis and the TEM observation. The X-ray diffraction shows the strength of sideband of cold-worked and aged alloy and that of the quenched and aged alloy are quite different. The modulation wavelength in deformed and aged alloy is obviously larger than that of the quenched and aged one. Our result is quite different from the Spooner and Lefever's obser-vation on the strength[2] of sideband. The TEM observation has found if the cold-worked sample is aged directly in 60 min , the black precipitates have already appeared in bright field image. And if the sample aged for 300 min, large precipitates will occur in the grain, which is consistent with Ditchck and Schwortz results[3] that black precipitates (Ni_3Sn) appear on Cu−10Ni−6Sn alloy quenched and aged for 16.5 h. As indicated above , the results show the spinodal decomposition on cold-worked and aged alloy is faster than that in quenched and aged allloy. In other words, the cold deformation accelerate the processes of spinodal

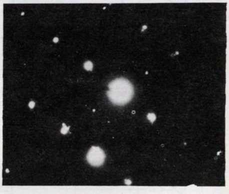


annealing+ageing, × 150,000



$L\lambda = 20$ mm · Å

cold−work+ageing, × 30,000



$L\lambda = 20$ mm · Å

Fig.4 Image of Bright field and diffraction pattern of alloys

decomposition in the Cu−9Ni−6Sn−0.3Ce alloy.

The cold deformation resulted in a high dislocation density alters chemical potential of the system. The free energy f_T of a quenched solution, including the elastic strain energy of the soluted atom, may be written as[4]

$$f_T = A[f(c) + k_1(d^2c/dx^2) + k_2(dc/dx)^2]dx \quad (4)$$

$$k_1 = \partial f/\partial(d^2c/dx^2) \quad (5)$$

$$k_2 = 0.5 \times \partial^2 f/\partial(dc/dx)^2 \quad (6)$$

where c—solute concentration (at.−%);

d_x—displacement;

A—system cross−section area

When the alloy is deformed, the density of dislocation is increased but the interaction force between the dislocation and the solute could be negligible. The cold deformation energy W is written as[5]

$$W = \frac{Eb}{4\pi\mu} n^{\frac{1}{2}} \rho^{\frac{1}{2}} \quad (7)$$

where E—Young's modulus;

μ—shear modulus;

b—displacement;

ρ—dislocation density;

n—dislocation number

The small entropy caused by deformation

is negligible. The free energy f_c caused by dislocation in the cross−section area A is

$$f_c = A\ \ W = \frac{AEb}{4\pi\mu} n^{\frac{1}{2}} \rho^{\frac{1}{2}} \qquad (8)$$

Total free energy F in the cold−worked Cu−9Ni−6Sn−0. 3Ce alloy is

$$F = f_T + f_c$$
$$= A\ [f(c) + k_1(d^2c / dx^2) +$$
$$k_2(dc / dx)^2]dx + \frac{AEb}{4\pi\mu} n^{\frac{1}{2}} \rho^{\frac{1}{2}} \qquad (9)$$

It is evident from equation (9) that the cold deformation energy is in direct proportion to dislocation density, it obviously increases the chemical potential and accelerates the processes of spinodal decomposition of the cold−worked alloy. The maximum strength of the alloy may be reached in advance. From equation (9), we can see that the strengthening is in proportion to the dislocation density, in other words, it is in proportion to the degree of cold deformation.

5 CONCLUSIONS

Through the study of the mechnical properties, resistivity, modulation, wavelength and micro-structures of the cold deformed and aged Cu−9Ni−6Sn−0.3Ce and that of the aged one without cold deformation, we have found that cold deformation energy will increase the system chemical potential. And it will obviously accelerate the spinodal decomposition. Furthermore, the plastic deformation leads to the strengthening of the material.

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texture and refine the grain size of the alloy, so the ductility of the alloy is improved.

(4) Step aging can make more Al_3Li / Al_3Zr compound particles, decrease the amount of equilibrium phases and the width of PFZ at grain boudaries, which leads to improvement in the ductility of the alloy.

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