EFFECT OF Y ON THE SPINODAL DECOMPOSITION RATE AND MECHANICAL PROPERTIES OF Cu–9Ni–6Sn ALLOY①

Deng, Zhongmin

Kunming Institute of Precious Metals, Kunming 650221, China

ABSTRACT

By measurement of mechanical and electrical properties, modulation wavelength, TEM techniques, etc., the effect of Y on the spinodal decomposition in Cu–9Ni–6Sn alloy has been studied. The results show that Y can accelerate spinodal decomposition in the alloy, hinder the growth of celluoid structurers occurring at grain boundaries, and improve the combination of strength and plasticity.

Key words: Cu–9Ni–6Sn spinodal decomposition Y

1 INTRODUCTION

A great deal of work has been done on the kinetics of spinodal decomposition. Cahn[1] first established a linear equation to describe this decomposition. Because the equation did not conform to experimental results, Tsakalakos and Hilliard[2], Langer, Boron and Miller[3] developed nonlinear diffusion equations. Cu–Ni–Sn alloys are typical elastic alloys strengthened by spinodal decomposition. In order to find wide application for these alloys in industry, much work has been done at home and abroad. Currently, this work is mainly focused on the effect of Y on the kinetics of spinodal decomposition in a Cu–9Ni–6Sn alloy, and aims to make use of the rich natural reserves of rare earth metals in our country to improve its over all performance.

2 EXPERIMENTAL

The alloy was melted by vaccum induction in an alumina crucible in an Ar atmosphere. The molten alloy was chill cast, homogenized at 820 ℃ for 6 h, water quenched, and cold-worked into wires of 0.19 mm diameter and sheets of 0.05 mm thickness, with intermediate annealing at 820 ℃.

0.19 mm diameter wires annealed at 820 ℃ for 1 h in charcoal, then water quenched. The quenched materials were aged at 350 ℃ for different times. The room temperature strength of the samples was measured using a FM3 pulling machine and the room temperature resistivity with a QJ19 electrical bridge.

0.8 mm thick samples were annealed at 820 ℃ for 2 h in charcoal, then water quenched. The quenched samples were aged at 350 ℃ for different times, then analysed using a D / max-rc diffractometer at 50 kV with CuKα radiation.

The 0.05 mm thick samples were annealed at 820 ℃ for 270 min in a H_2 atmosphere. The annealed samples were aged at 350 ℃ using a DWT702 autocontroller to control the temperature. The film samples were thinned and punched with a mixture of acetic, nitric and phosphoric acids, then observed on a JEM–

①Manuscript received Oct. 23, 1992

2000EX TEM.

3 RESULTS

3.1 *Effect of* Y *on Mechanical Properties and Resistivity*

Fig. 1 shows the time dependence of mechanical properties at 350 ℃. It is evident that the σ_b, δ of the alloy with Y are higher than those without Y. The experimental results indicate that Cu–9Ni–6Sn aged for 960 min is very brittle, but the alloy with 0.3% Y aged for the same time is not so brittle.

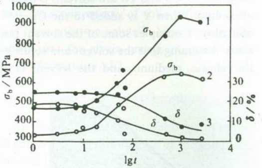


Fig. 1 The time dependence of mechanical properties at 350 ℃

1, 3—with Y; 2, 4—without Y

Fig. 2 shows the time dependence of ρ. From it, we have:

for Cu–9Ni–6Sn alloy,

$$\rho=\rho_o\exp(-0.002{,}029\ 1\ t) \quad (1)$$

for Cu–9Ni–6Sn–0.3Y,

$$\rho_t=\rho_o\exp(-0.002{,}542\ t) \quad (2)$$

where ρ_0 is the resistivity of the quencned sample, $\mu\Omega\cdot$ cm, and t is aging time, min.

3.2 *Effect of* Y *on Modulation Wavelength*

Fig. 3 shows the time dependence of wavelength. From it, it is evident that the modulation wavelength of the alloy increases rapidly when the aging time is shorter than 60 min, then increase much more slowly when the time is longer than 300 min. The modulation wavelength of the alloy with Y is greater than that of the alloy without Y.

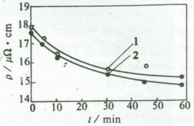


Fig. 2 The time (t) dependence of the resistivity (ρ)

1—without Y; 2—with Y

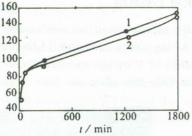


Fig. 3 The aging time (t) dependence of the modulation wavelength (λ)

1—with Y; 2—without Y

3.3 TEM *Observation After Aging*

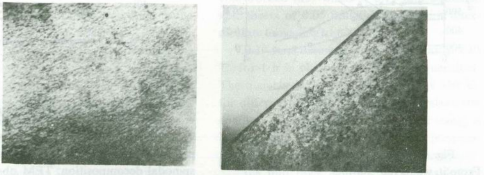
Aging at 450 ℃ and below results in a ripplelike structure which characterizes alloys spinodal decomposition. TEM observation of the Cu–9Ni–6Sn, with and without Y, aged at 350 ℃ for 10 min indicates that in the bright field images there exist visible modulated structure. No diffraction speckles of the second phase appear in the diffraction patterns of the samples. When the samples aged at 350 ℃ for 60 min, the modulated structures of the alloys are more visible, and diffraction patterns of the alloys show diffraction speckles of the second phase. Coarsening was observed in the bright field images of the samples aged at 350 ℃ for 300 min. The coarsening and diffraction speckles of the second phase in the alloy with Y are clearer when compared to the alloy without Y. The bright field images in the samples with and without Y aged for 60 min and 300 min, are shown in Figs. 4 and 5 respectively.

The celluoid structure and its distribution in the alloy, with and without Y, aged for 60 min, are shown in Fig. 6. From the figure, we consider that the microstructures observed in the alloy with Y can be attributed to the improvement in its spinodal decomposition and coarsening kinetics and hindrance in the growth of celluoid structure occurring at grain boundries.

4 DISCUSSION

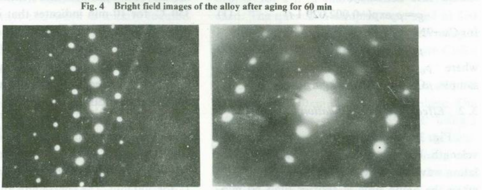
By measurement of mechanical properties, X–ray diffraction and TEM techniques, the effect of Y on the spinodal decomposition of Cu–9Ni–6Sn alloy has been studied. The results show that Y can increase the strength and extensibility of the alloy. Y can change the kinetics of spinodal decomposition and hinders the growth of celluoid occurring at grain boundaries.

The mechanism of the effect of Y on spinodal decomposition remains to be investigated. We guess that it is concerned with atomic radius. The atomic radii of the investigated alloy are $r_{Cu} = 1.276$ Å, $r_{Ni} = 1.243$ Å, $r_{Sn} = 1.58$ Å, $r_Y = 1.801$ Å. The results of X–ray diffraction analysis show that Y does not alter the crystal lattice of the Cu–9Ni–6Sn alloy. We assume that Cu and Ni are solvent, Sn and Y are solute. When Y is added to the Cu–9Ni–6Sn alloy, Y occupies some of the solvent positions. Assuming that the solvent and solute are the elastic medium, and the solvent is an



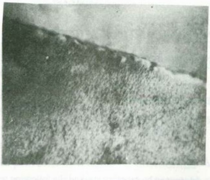
Cu–9Ni–6Sn (× .000) Cu–9Ni–0.3Y (× 45,000)

Fig. 4 Bright field images of the alloy after aging for 60 min

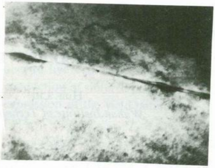


Cu–9Ni–6Sn, $L\lambda = 20 / mm \cdot$ Å Cu–9Ni–6Sn–0.3Y, $L\lambda = 20 / mm \cdot$ Å

Fig. 5 Diffraction patterns of the alloy aging for 300 min



Cu–9Ni–6Sn (×90,000)



Cu–9Ni–0.3Y (×90,000)

Fig. 6 Celluoid structure and its extension of the alloy aging for 60 min

isotropic, continuous medium, Friedel calculated the strain energy of solid solution of the high concentration solute[4]. Moreover, it is assumed that the strain energy is equal to the heat of formation(ΔH)

$$W=\triangle H=\frac{6\pi\bar{r}\triangle^{2}}{(1+\alpha)\bar{x}}c(1-c) \qquad (3)$$

Considering the organic entropy of the solid solution, the free energy F of the solid solution can be written as

$$F\approx\frac{6\pi\bar{r}\triangle^{2}}{(1+\alpha)\bar{x}}c(1-c)+ KT[c\ln c+(1-c)\ln(1-c)] \qquad (4)$$

Where $\Delta=r_B-r_A$, r_B and r_A are the radii of the solute atom and solvent atom respectively; W_A and W_B are the sums of the strain energies of the solvent lattice and the solute atom lattice respectively; $\bar{r}$ is the average solute atom and solvent atom radius; $\bar{x}$ is the average compressibility; c is the solute concentration. Because the radius of the Y atom is larger than that of the Sn atom, Y added to the Cu–9Ni–6Sn not only alters the solute concentration but also leads to lattice distortion, which is caused by the difference in size between Y and the solvent atom. The distortion increases the chemical potential of the system. Thus, Y can change the kinetics of the spinodal decomposition in Cu–9Ni–6Sn alloy, accelerating the modulation decomposition.

The dependence of the modulation wavelength on aging time can be written as[5]

$$\lambda_3-\lambda_0^3=k(t-t_0) \qquad (5)$$

where λ_0 is the initial modulation wavelength and k is a constant. We found that the relationship between λ and t is consistent with equation (6) after the Cu–Ni–Sn alloys has been aged for 300 min.

$$\lambda_3-\lambda_0^3=k\,t \qquad (6)$$

5 CONCLUSIONS

Y can change the kinetics of spinodal decomposition in the Cu–9Ni–6Sn alloy, accelerate modulation decomposition, hinder the growth of celluoid structure occurring at grain boundaries, raise the strength and plasticity of the alloy, and improve the combination of strength and plasticity. The mechanism of the effect of Y on spinodal decomposition need further investigation.

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