Influence of Solution-Treatment Conditions on the Cellular Precipitation in Si-Doped Cu-10Ni-8Sn Alloy

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The influence of solution-annealing conditions (temperature and time) on the nucleation and growth of grain boundary cells in the 0.2%Si-doped Cu-10%Ni-8%Sn alloy on aging at 723 K was investigated by the quantitative metallographic method. The hardness change in the matrix during aging at 723 K was scarcely affected by the solution-annealing conditions. However, the nucleation and growth of the cell during aging was remarkably affected by the solution-annealing conditions. When the solution-annealing temperature or time was increased, the suppressing effect of Si on the cellular precipitation was decreased. The $\text{Ni}_{31}\text{Si}_{12}$ phase particles which existed in the matrix grains and grain boundaries in the as-quenched specimen were coarsened with increasing solution-annealing temperature or time. Therefore, it is suggested that in the specimen solution-annealed at a higher temperature or for a longer time, the effects that the $\text{Ni}_{31}\text{Si}_{12}$ phase particles occupy the nucleation sites of the cells in the grain boundaries and suppress the migration of the advancing boundaries of the cells on aging were decreased.

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I. Introduction

It is well known that the cellular precipitation in various alloys is suppressed remarkably by the addition of small amounts of additives⁽¹⁾. For example, the addition of Co, Ni, or Fe to Cu-Be alloys is very effective on the suppression of the cellular precipitation in these alloys⁽²⁾⁻⁽⁴⁾. However, the reasons why the doped-elements suppress the cellular precipitation have not been clarified sufficiently yet. The present authors⁽⁵⁾ have previously proposed such a mechanism as follows: The atoms of the doped element segregate in the grain boundaries and occupy the nucleation sites of cells, otherwise the fine insoluble compound particles, which consist of the doped-element and the solvent (or solute) element, precipitate in the grain boundaries and matrices in a as-quenched state and then suppress the nucleation and growth of the cells on the subsequent aging. Moreover, they have performed a series of studies⁽⁶⁾⁻⁽⁹⁾ in order to confirm the above mechanism. In the case of Si addition to a Cu-10%[†]Ni-8%Sn alloy, they have elucidated that the doped-Si combined dominantly with Ni and precipitated as fine $\text{Ni}_{31}\text{Si}_{12}$ phase particles in the grain boundaries and matrix grains in the water-quenched specimen and as a result, these fine $\text{Ni}_{31}\text{Si}_{12}$ particles suppressed remarkably the nucleation and growth of the cells⁽⁹⁾.

Therefore, it is assumed that the largeness of the suppressing effect by the doped-element (Si) depends on the shape and distribution of these $\text{Ni}_{31}\text{Si}_{12}$ phase particles in

the as-quenched specimen. That is, the suppressing effect probably depend on the solution-annealing temperature and time which will influence the shape and distribution of the $\text{Ni}_{31}\text{Si}_{12}$ particles. Therefore, the present work was aimed to examine the influences of the solution-annealing temperature and time on the nucleation and growth of the grain boundary cells of the Cu-10%Ni-8%Sn alloy, and to confirm the above mechanism in more detail.

As reported in the several papers⁽¹⁰⁾⁻⁽¹²⁾, the Cu-9-10%Ni-6-8%Sn alloy decomposed spinodally and formed a modulated structure with Sn-rich zone and Sn-lean zone on aging below 723 K after water-quenching from 1123 K to 1173 K. With the progress of aging, a metastable γ' -(Cu·Ni)₃Sn phase with D0₂₂ structure was formed in the Sn-rich zone and changed to the γ -(Cu·Ni)₃Sn phase with D0₃ structure which is incoherent to the matrix. As the Cu-Ni-Sn alloy is extremely hardened by the formation and growth of the γ' phase, this alloy is being used commercially as spring materials⁽¹³⁾⁽¹⁴⁾.

However, on aging of this alloy, the cells with the lamellar structure of the equilibrium γ and α phases formed at the grain boundary and progressed into the matrices where the γ' phase had precipitated⁽¹⁵⁾. The growth of these grain boundary cells brought the decreases in the strength and corrosion resistance. Therefore, in order to suppress the formation and growth of the cells, the present authors have already examined the effects of several additives containing Si and reported that the addition of Si remarkably suppressed the formation and growth of the grain boundary cells by the mechanism described above⁽⁹⁾.

II. Experimental

Chemical compositions of the alloys used are shown in

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[†] In this paper, the composition is denoted by mass%.

Table 1 Chemical compositions of alloys (mass%).

Nominal	Cu	Ni	Sn	Si	Fe
Cu-10Ni-8Sn	Bal.	9.79	8.10	—	0.003
Cu-10Ni-8Sn-0.2Si	Bal.	9.86	7.89	0.22	0.004

Fig. 1 Changes in the mean grain size of Cu-10%Ni-8%Sn-0.2Si alloys during solution-annealing at 1123 and 1173 K after 70% cold-rolling.

Table 1. These alloys were made by melting electrolytic copper (99.95%), high-purity nickel (99.95%), high-purity tin (99.99%) and a Cu-15%Si mother alloy in high-purity alumina crucibles in an Ar atmosphere. These alloy ingots were homogenized at 1123 K and then

cut into plates 3 mm in thickness. These plates were cold-rolled by 70% and shaped into a suitable form for the following measurements. These specimens were quenched after solution-annealing at 1123 and 1173 K for 3.6 and 28.8 ks. The changes in the mean grain size of the Si-free and 0.2%Si-doped alloys during solution-annealing are shown in Fig. 1. The grain growth of the 0.2%Si-doped alloy was suppressed by the $\text{Ni}_{31}\text{Si}_{12}$ particles insoluble to the matrix at the solution-annealing temperatures⁽⁹⁾.

The specimens with the mean grain size shown by A, B, C and D in Fig. 1 were aged at 723 K and then examined by optical and electron microscopy, and a micro-Vickers hardness tester. The measurements of the width of the cells were carried out on the optical micrographs with the magnification of $150\times$. The maximum and mean values among the widths of 50 single-seam cells, respectively. The values of N_C/N_T , the ratio of the number of the grain boundaries with the cell to the number of the total grain boundaries, were measured also by using the same optical micrographs as described above. In order to examine the shape and distribution of the $\text{Ni}_{31}\text{Si}_{12}$ phase particles, TEM observation was carried out about the AC-carbon two-step replicas of the specimens (A, B, C and D) quenched after solution-annealing. The hardness was measured by use of a micro-Vickers hardness tester with the load of 0.98 N.

III. Results

Figure 2 shows the optical microstructures of the specimens (A, B, C and D) aged at 723 K for 4.8 ks after

Fig. 2 Optical microstructures of Cu-10%Ni-8%Sn-0.2%Si specimens aged at 723 K for 4.8 ks after solution-annealing at 1123 K for 3.6 ks (a) and 28.8 ks (b) or at 1173 K for 3.6 ks (c) and 28.8 ks (d).

solution-annealing at 1123 K and 1173 K for various times. It is evident from this figure that the higher the solution-annealing temperature, the wider became the cell width and also that the longer the solution-annealing time, the wider became the cell width.

Figure 3 shows the changes in maximum cell width of four specimens during aging at 723 K. The higher the solution-annealing temperature (and the longer the solution-annealing time), the earlier became the cell formation and the larger the cell growth rate. As a result, the cell growth rate of the 0.2%Si-doped alloy approached that of the Si-free alloy. Namely, the effect of the Si addition on the suppression of the cellular precipitation was decreased with increasing time and temperature of solution-annealings.

A similar result was obtained for the changes in the mean cell width as shown in Fig. 4. The higher the solution-annealing temperature (and the longer the solution-annealing time), the earlier became the cell formation and the larger the cell growth rate.

Figure 5 shows the changes in N_C/N_T with progress of aging. The increase in N_C/N_T was remarkable especially in the specimens which were solution-annealed for a longer time and at a higher temperature. As a result, the

Fig. 3 Changes in the maximum cell width of Cu-10%Ni-8%Sn-0.2%Si specimens solution-annealed at 1123 and 1173 K for 3.6 ks and 28.8 ks on aging at 723 K.

Fig. 4 Changes in the mean cell width of Cu-10%Ni-8%Sn-0.2%Si specimens solution-annealed at 1123 and 1173 K for 3.6 ks and 28.8 ks on aging at 723 K.

Fig. 5 Changes in N_C/N_T , the ratio of the number of the grain boundaries with cells to the number of the total grain boundaries, on aging of Cu-10%Ni-8%Sn-0.2%Si specimens solution-annealed at 1123 and 1173 K for 3.6 ks and 28.8 ks.

Fig. 6 Changes in hardness of the matrices and cells in Cu-10%Ni-8%Sn-0.2%Si specimens solution-annealed at 1123 and 1173 K for 3.6 ks and 28.8 ks on aging at 723 K.

tendency of the increase in N_C/N_T in the 0.2%Si-doped alloy was similar to that in the Si-free alloy. It is clear from this figure that the effect of the Si addition on the suppression of the cell formation was decreased with increasing-annealing temperature and time.

Figure 6 shows the hardening curves of the matrices and the cells in the four specimens on aging at 723 K. Regardless of the solution-annealing conditions, the hardness of the four specimens changed nearly in the same manner during aging.

IV. Discussion

The effect of the doped-Si on the suppression of the cellular precipitation in the Cu-10%Ni-8%Sn alloy was decreased with increasing solution-annealing temperature and time. We will discuss the reasons from the viewpoint of the nucleation and growth of the cell.

First, we will discuss the effect of the solution-annealing temperature and time on the cell growth. The growth of the cell can be described generally by

$$G = M \cdot P (P_C + P_S + P_I + P_P)^{(16)},$$

where G is the growth rate of the cell, M is the mobility of the advancing boundary of the cell, and P is the driving force. The driving force (P) can be divided into four

small parts (P_C , P_S , P_I and P_P). The driving force P_C is the chemical driving force due to the difference in the solute concentration between the matrix and the cell, P_S is the driving force due to the strain energy difference between the precipitates in the matrix and the cell, P_I is the driving force due to the interfacial energy difference between the precipitates in the matrix and the cell, and P_P is the retarding force (back driving force) to the migration of the advancing boundary of the cell due to the fine particles in the matrix and grain boundaries. In this study, the hardness changes of the matrices of the four specimens during aging, as shown in Fig. 6, were nearly the same; namely the hardness change was not affected by the solution-annealing conditions (temperature and time). Moreover, the peak hardness values of the four specimens were nearly the same. From these facts, it is considered that the value of ($P_C + P_S + P_I$) is scarcely affected by the difference in the solution-annealing condition. Nevertheless, the growth rate of the cell (G) was increased in the specimens solution-annealed at a higher temperature and for a longer time. This fact means that the mobility of the advancing boundary (M) was increased or the retarding force (P_P) to the migration of the advancing boundary of the cell was decreased.

As described in the previous paper⁽⁹⁾, the following mechanism was proposed as the mechanism by which the doped-Si suppresses the nucleation and growth of the cell. (1) The doped Si atoms segregated in the grain boundaries in the as-quenched specimen and suppressed the nucleation and growth of the cell on the subsequent aging. (2) The doped-Si combined dominantly with the Ni atoms and formed the fine $\text{Ni}_{31}\text{Si}_{12}$ phase particles in the as-quenched specimen. Such fine $\text{Ni}_{31}\text{Si}_{12}$ phase particles in the grain boundaries and matrices occupied the formation sites of the cells in the grain boundaries and suppressed the growth of the advancing boundaries on aging. Here, we will discuss the effect of the solution-annealing conditions (temperature and time) on the grain boundary segregation of the Si atoms. Since the solid solubility is generally increased with increasing temperature, the grain boundary segregation will be decreased. Therefore, the higher solution-annealing temperature will bring the decrease in the grain boundary segregation of the Si atom. As a result, the grain boundary mobility (M) will be increased and the retarding force to the grain boundary migration (P_P) due to the solute drag effect of the Si atoms in the grain boundaries will be decreased. On the other hand, in this study the increase in solution-annealing time does not seem to affect so much the grain boundary segregation on the solute atom because the solution annealing time of 3.6 ks at 1123 K is considered to be sufficient for the Si atoms to segregate in the grain boundaries. However, in this study, we could not confirm the grain boundary segregation of the Si atoms.

Next, we will discuss the influence of the solution-annealing temperature and time on the shape and number of the insoluble $\text{Ni}_{31}\text{Si}_{12}$ particle in the as-quenched specimen. If the solution-annealing temperature and time are increased, these $\text{Ni}_{31}\text{Si}_{12}$ particles will be coarsen-

ed and the number of the particles in the matrices and grain boundaries will be decreased. It will lead to the increase in the mobility of the grain boundary (M) and the decrease in the retarding force to the grain boundary migration (P_P).

In order to confirm this point, the shape and amount of the $\text{Ni}_{31}\text{Si}_{12}$ particle in the as-quenched specimen were checked by TEM. The result is shown in Fig. 7. As seen from this figure, the $\text{Ni}_{31}\text{Si}_{12}$ particles were coarsened with increasing solution-annealing temperature and time. The mean radius (r) of the $\text{Ni}_{31}\text{Si}_{12}$ particles could be measured from this figure, but the volume fraction (f) of the particles could not be measured precisely because of experimental difficulties. Therefore, in Table 2, the measured mean particle radius (r) and the estimated volume fraction (f) of the $\text{Ni}_{31}\text{Si}_{12}$ particles are shown. The measured particle radius (r) was increased remarkably depending on the solution-annealing temperature and time. On the other hand, the volume fraction (f) was roughly estimated as 0.008 by assuming that almost all the doped Si atoms, 0.22 mass%, precipitated as the $\text{Ni}_{31}\text{Si}_{12}$ phase particles at the solution-annealing temperatures of 1123 and 1173 K. The retarding force to the grain boundary migration (P_P) was calculated by using these values. When the fine particles distribute homogeneously in the matrix and grain boundaries, the retarding force (P_P) is denoted⁽¹⁷⁾⁽¹⁸⁾ by

$$P_P = 3\sigma f / 2r.$$

Here, the r and f are the radius and volume fraction of fine particles, respectively. The σ is the grain boundary energy. Now, if we substitute the above values to the r and f , and use the value of the grain boundary energy of Cu, 0.6 J/m^2 ⁽¹⁹⁾, as the value of the σ , we can obtain 1.4, 0.58, 0.54 and $0.36 \times 10^6 \text{ N/m}^2$ as the value of the P_P of four specimens (A, B, C and D). These calculated values are well consisted with the cell growth behaviours shown in Figs. 2–4. Namely, the cell growth rate (G) is smaller in the specimen with larger retarding force (P_P).

The precise value of the chemical driving force (P_C) for the cell boundary migration in the Cu–10%Ni–8%Sn alloy could not be obtained, but the approximate value was roughly calculated to be $5 \times 10^7 \text{ N/m}^2$. In an Al–5%Zn alloy, the value of about 10^7 N/m^2 has been reported⁽¹⁸⁾. In this study, the values of the P_S and P_I could not be obtained. Therefore, if it is assumed that the ($P_C + P_S + P_I$) is nearly equal to the P_C , the value of the ($P_C + P_S + P_I$) may be about 10^7 N/m^2 . This value is much larger than the values of the calculated retarding force, $1.4 - 0.4 \times 10^6 \text{ N/m}^2$. Namely, this means that the $\text{Ni}_{31}\text{Si}_{12}$ particles will scarcely suppress the cell boundary migration in any specimen. However, it has been reported⁽²⁰⁾, that in the case of the inhomogeneous distribution of the fine particles, such as the fine particles precipitate dominantly in the grain boundaries, the retarding force (P_P) becomes significantly larger than in the case of the homogeneous distribution of the particles. Since in the Cu–10%Ni–8%Sn–Si alloys, the $\text{Ni}_{31}\text{Si}_{12}$ particles tend to precipitate dominantly in the grain bound-

Fig. 7 TEM microstructures of the AC-carbon two step replicas of the Cu-10%Ni-8%Sn-0.2%Si specimens solution-annealed at 1123 K for 3.6 ks (a) and 28.8 ks (b) or at 1173 K for 3.6 ks (c) and 28.8 ks (d).

Table 2 The measured values of the mean radius (r) and the estimated values of the volume fraction (f) of the $\text{Ni}_{31}\text{Si}_{12}$ particles in Cu-10%Ni-8%Sn-0.2%Si specimens solution-annealed at 1123 and 1173 K, and the retarding force to the cell boundary migration (P_p) calculated by using the equation $P_p = 3\sigma f / 2r$. ($\sigma = 0.6 \text{ J/m}^2$).

Specimens	Solution-annealing temperature and time	r (nm)	f^*	P_p (N/m^2)
A	1123 K - 3.6 ks	5.3	0.008	1.4×10^6
B	— 28.8 ks	12.5	0.008	0.58
C	1173 K - 3.6 ks	13.3	0.008	0.54
D	— 28.8 ks	20.0	0.008	0.36

*Estimated values.

aries⁽⁹⁾, the actual value of P_p in each specimen must be much larger than that in Table 2. Namely, it is considered that the growth rate of the cell (G) must have been affected largely by the size, distribution and volume fraction of the insoluble particles ($\text{Ni}_{31}\text{Si}_{12}$) in the matrix and grain boundaries.

Finally, we will discuss the effect of the solution-annealing conditions on the nucleation of the cell. As seen from Fig. 7, the $\text{Ni}_{31}\text{Si}_{12}$ phase particles in the as-quenched specimens became coarser with increasing solution-annealing temperature and time. From these facts, it seems that the number of the $\text{Ni}_{31}\text{Si}_{12}$ particles in the grain boundaries is decreased with increasing solution-annealing temperature and time. As a result, the possibility that the $\text{Ni}_{31}\text{Si}_{12}$ particles occupy the nucleation sites of the cells in the grain boundaries may be reduced. Consequently, the effect of Si addition on the suppression of the nucleation of the cells will be decreased.

V. Conclusion

The influence of solution-annealing conditions (temperature and time) on the nucleation and growth of grain boundary cells in the 0.2%Si-doped Cu-10%Ni-8%Sn alloy on aging at 723 K was investigated. The results obtained are as follows:

(1) On aging at 723 K, the hardness change in the matrix was scarcely affected by the solution-annealing conditions.

(2) when the solution-annealing temperature or time was increased, the nucleation and growth of the cell were stimulated. Namely, the suppressing effect of Si on the cellular precipitation was decreased.

(3) The $\text{Ni}_{31}\text{Si}_{12}$ phase particles existing in the as-quenched specimen were coarsened with increasing solution-annealing temperature or time. Therefore, it is suggested that in the specimen solution-annealed at a higher temperature or for a longer time, the effects that the $\text{Ni}_{31}\text{Si}_{12}$ phase particles occupy the nucleation sites of the cells in the grain boundaries and suppress the migration of the advancing boundaries of the cells on aging were decreased.

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