Effects of Co, Ni and Ti Additions on the Cellular Precipitation in Cu-2%Be Alloy

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The effects of additions of 0.1–2.0% of Co, Ni and Ti on the cellular precipitation in a Cu-2 mass%Be alloy were investigated by the quantitative metallographic method.

The addition of Co, Ni and Ti hastened the start of the precipitation of γ' phase in the matrix and increased slightly the maximum hardness. These elements refined the grain size of the as-quenched specimens and also suppressed remarkably the cell growth on the subsequent aging. The quantitative correlation was found out between the suppressing effect of these elements on the grain growth in the Cu-2%Be alloy at solution-treatment temperature and that on the cell growth at the aging temperature. In the as-quenched specimens containing Co, Ni and Ti, fine insoluble compound particles, BeCo, BeNi and Be_(10+n)Ti_n, were detected, respectively. It is considered, therefore, that these fine insoluble particles suppressed the grain growth at the solution-treatment temperature and also suppressed the migration of the advancing boundary of the cell at the aging temperature.

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I. Introduction

Cellular precipitation occurs very often on aging of supersaturated solid solution alloys. Cellular precipitation generally progresses by the following mechanism: A grain boundary cell with a lamellar structure which consists of a nearly equilibrium precipitate phase and α -phase, nucleates in a grain boundary and it grows into the matrix where nonequilibrium phases are precipitating.

As the growth of the cell degrades the strength and corrosion resistance of the alloy, many studies have been carried out to find the methods to suppress the growth of the cell, for example, studies on the effects of cold rolling^{(1)–(3)}, applied stress^{(4)–(5)}, solution-treatment temperature⁽⁶⁾, aging temperature⁽⁷⁾, grain boundary structure⁽⁸⁾ and additional elements^{(9)–(14)}. Through these studies, it has been clarified that the addition of the third elements to the binary alloys is especially effective to suppress the cell growth⁽¹⁵⁾. In Cu-Be alloys, additions of Co, Ni and Ti are very effective^{(9)–(11)–(14)–(16)}. However, the reason why the addition of such elements is effective in suppressing the cell growth have not been clarified sufficiently yet.

The present authors⁽¹⁶⁾ previously proposed the following mechanism as the main suppressing mechanism: (1) A part of the doped element atoms segregates in the grain boundaries, occupies the nucleation sites of cells and suppresses the growth of the cell by the solute-drag effect. (2) The doped-element and the solute (or solvent) element combine dominantly and form the fine insoluble compound particles in the grain boundaries and matrices in

the as-quenched state, resulting in suppressing the nucleation and growth of the cells on the subsequent aging. Moreover, they have performed a series of studies^{(17)–(20)} in order to confirm the above mechanism. In the cases of boron additions to Cu-Be and Ni-Sn alloys, doped boron atoms seem to suppress the nucleation and growth of the cell by segregating in the grain boundary^{(17)–(18)}. In the case of Si addition to a Cu-10 mass%Ni-8 mass%Sn alloy, they elucidated that the doped-Si combined dominantly with Ni and existed as fine insoluble Ni₃₁Si₁₂ phase particles in the grain boundaries and matrices in the water-quenched specimen and as a result, these fine Ni₃₁Si₁₂ particles suppressed remarkably the nucleation and growth of the cells on the subsequent aging^{(19)–(20)}.

The aim of this study is to clarify more sufficiently the reason why Co, Ni and Ti elements doped to a Cu-Be alloy remarkably suppress the nucleation and growth of the cell. In the following paper⁽²¹⁾, we will report as for the effects of doped elements on the cellular precipitation in a Cu-Ni-Sn alloy.

Many reports^{(22)–(33)} have been published on the precipitation process in the Cu-Be binary alloy, and a sequence of the precipitation within the matrix is summarized briefly as follows; α -supersaturated solid solution $\rightarrow$ G.P. zone $\rightarrow$ γ' intermediate phase $\rightarrow$ γ -(CuBe) equilibrium phase. This alloy is hardened excellently by the precipitation of the γ' phase. However, with progress of aging at low temperatures, the cell with a lamellar structure which consists of the nearly equilibrium α and γ phases progresses from grain boundaries into the matrix and engulfs nearly completely the matrix.

II. Experimental

The amount of the element (Co, Ni or Ti) doped to a Cu-2 mass%Be standard alloy is 0.1, 0.3, 0.5, 0.7, 1.0 and 2.0 mass%. Chemical compositions of the typical alloys are shown in Table 1. Each alloy was prepared by melting electrolytic copper (99.95%), pure nickel (99.99%), Cu-4%Co and Cu-24.5%Ti master alloys in a high purity alumina crucible under argon atmosphere. These alloy ingots were homogenized at 1093 K and then cut into plates 3 mm in thickness. These plates were cold-rolled by 50% and shaped into a suitable form for the following measurements.

These specimens were water-quenched after solution-treatment at 1093 K for 3.6 ks and then aged at 623 K. Hardness testing, optical and electron microscopic obser-

vations and X-ray analysis were carried out for the aged specimens. The hardness was measured by use of a micro-Vickers hardness tester with the load of 0.98 N. The measurements of the width of the cells were carried out on the optical micrographs with the magnification of 150 and 600X. The X-ray analysis was done by an X-ray diffractometer with a Cu target. TEM observation of as-quenched specimens was carried out using the AC-carbon two-step replicas of the specimens. TEM observation of the aged specimens was undertaken for the thin films of the specimens.

III. Results and Discussion

Figure 1 shows typical microstructures of Co-doped alloys aged at 623 K. The crystal grain of the as-quenched alloys was refined with increasing amount of the additions. The cell growth of these alloys at 623 K was also suppressed with increasing amount of the additions.

Figures 2-4 show the changes in the mean cell width of Cu-2%Be alloys containing Co, Ni and Ti on aging at 623 K. By the addition of Co, Ni or Ti, the start of the cell growth was retarded and the growth rate of cell was decreased. Especially the effect of Co addition was remarkable.

Figures 5-7 show the hardness changes of Cu-2%Be alloys containing Co, Ni and Ti on aging at 623 K. The start of the hardening in the matrix was hastened by the addition of Co, Ni or Ti. In the case of Co or Ni addition, 0.3% of addition hastened it most remarkably and in the case of Ti addition, 0.5% of addition is the most. Since the hardening in the matrix of the Cu-2%Be alloy on aging at 623 K is mainly caused by the precipitation of

Table 1 Chemical compositions of typical alloys used (mass%).

Nominal	Cu	Be	Co	Ni	Ti	Fe
Cu-2Be	Bal.	2.01	<i>t</i>	<i>t</i>	<i>t</i>	0.04
-0.1Co	Bal.	1.98	0.09	<i>t</i>	<i>t</i>	0.04
-0.5Co	Bal.	1.97	0.51	<i>t</i>	<i>t</i>	0.04
-1.0Co	Bal.	2.02	0.97	<i>t</i>	<i>t</i>	0.03
-0.1Ni	Bal.	1.98	<i>t</i>	0.11	<i>t</i>	0.04
-0.5Ni	Bal.	1.99	<i>t</i>	0.49	<i>t</i>	0.03
-1.0Ni	Bal.	2.01	<i>t</i>	0.99	<i>t</i>	0.04
-0.1Ti	Bal.	1.97	<i>t</i>	<i>t</i>	0.08	0.03
-0.5Ti	Bal.	2.03	<i>t</i>	<i>t</i>	0.48	0.04
-1.0Ti	Bal.	1.98	<i>t</i>	<i>t</i>	0.98	0.04

(*t* < 0.001 mass%)

Fig. 1 Optical microstructures of Cu-2%Be-X%Co alloys aged at 623 K for 4.8 ks. (a) Cu-2%Be, (b) -0.1%Co, (c) -0.3%Co and (d) -0.5%Co.

Fig. 2 Changes in the mean cell width of Cu-2%Be-Co alloys on aging at 623 K.

Fig. 4 Changes in the mean cell width of Cu-2%Be-Ti alloys with progress of aging at 623 K.

Fig. 3 Changes in the mean cell width of Cu-2%Be-Ni alloys during aging at 623 K.

Fig. 5 Hardness changes of Cu-2%Be-X%Co alloys on aging at 623 K after quenching from 1093 K.

the γ' phase⁽²²⁾⁽²⁹⁾, the additions of these elements is considered to hasten the precipitation of the γ' phase. However, the excess addition weakens the hastening effect. The initial hardness value in the as-quenched state and the maximum hardness value after aging increased slightly by the addition of these elements. The increase in the initial hardness value in the as-quenched state by the addition of these elements will be due to the existence of fine insoluble particles which consist of Be and these

elements (Co, Ni and Ti) as shown later.

Figure 8 shows the relation between the initial growth rate of the cell in the Cu-2%Be alloys containing additives (Co, Ni and Ti) on aging at 623 K and the amounts of additives. The growth rate of cells in the alloys containing these additives decreased remarkably with increasing amount of additives and kept a nearly constant value by the addition beyond 0.5%.

Figure 9 shows the relation between the mean grain size of the as-quenched Cu-2%Be alloys containing additives (Co, Ni and Ti) and the amounts of additives. The mean grain sizes of these alloys were refined with increasing amount of additives. However, on the addition of 0.5% or more, they kept nearly the constant value (about

Fig. 6 Hardness changes of Cu-2%Be-X%Ni alloys during aging at 623 K.

Fig. 7 Hardness changes of Cu-2%Be-X%Ti alloys with progress of aging at 623 K.

10 μm).

Figure 10 shows the relation between the mean grain size of the as-quenched Cu-2%Be alloys containing Co, Ni and Ti and the initial growth rate of cells on aging at 623 K. It is evident from this figure that the specimen, which has the smaller grain size in the as-quenched state, shows the smaller growth rate of cell on aging at 623 K. This fact suggests that the mechanism by which the additives suppress the migration of the advancing boundaries of cells at aging temperature is nearly the same as the mechanism by which the additives suppress the grain boundary migration at the solution treatment temperature. Namely, the reason must be due to the grain boundary segregation of additive elements or the existence of the fine compound particles which consist of the additive elements (Co, Ni or Ti) and the solute element (Be).

The growth rate of the cell is generally described as follows⁽⁷⁾:

Fig. 8 Relation between the initial growth rate of cell of Cu-2%Be alloys containing additives (Co, Ni and Ti) at 623 K and the amounts of additives (X).

Fig. 9 Relation between the mean grain size of the as-quenched Cu-2%Be alloys containing additives (Co, Ni and Ti) and the amounts of additives (X).

$$G = M \cdot P (P_C + P_S + P_I - P_P)$$

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 for the cell growth. The driving force, P , can be divided to P_C , P_S , P_I and P_P , where P_C is the chemical driving force due to the solute concentration difference between the matrix and the cell, and P_S is the driving force due to the strain energy difference between the matrix and the cell, P_I is the driving force due to the inter-

Fig. 10 Relation between the mean grain size of the as-quenched Cu-2%Be alloys containing Co, Ni and Ti and the initial growth rate of cell on aging at 623 K.

facial energy difference between the matrix and the cell, and P_p is the resistance force to the grain boundary migration caused by the insoluble particles in the matrices and the grain boundaries. In this study, the hardening in the matrix was hastened by the addition of Co, Ni or Ti. In general, the hastening of the precipitation in the matrix may leads to the rapid decrease in chemical driving force (P_c) for cell growth. On the other hand, it is well known that the strain energy and the interfacial energy in the matrix increase remarkably by the precipitation of the γ'

Fig. 12 X-ray diffraction patterns of the as-quenched Cu-2%Be alloys containing Co, Ni and Ti.

phase in the Cu-Be-X alloys⁽¹⁶⁾. Therefore, the rapid decrease in the chemical driving force (P_c) due to the hastening of the precipitation of the γ' phase seems to have been compensated by the rapid increase in the driving force due to the strain energy and interfacial energy

Fig. 11 TEM observations of the AC-carbon two-step replica of Cu-2%Be alloys containing Co, Ni and Ti. (a) Cu-2%Be, (b) -0.3%Co, (c) -0.3%Ni and (d) -0.3%Ti.

differences between the matrix and cell ($P_S + P_I$), and the sum of the driving force ($P_C + P_S + P_I$) seems to have not been so largely decreased by the additions of Co, Ni and Ti. From the above inference and the result of Fig. 10, it is considered that the remarkable decrease in the cell growth rate by the additions of these elements must have been caused mainly by the increase in the resistance force (P_P).

In order to detect the fine compound particles which must have suppressed the formation and growth of the cell, AC-carbon two-step replicas of the as-quenched specimens containing Co, Ni and Ti were prepared. Figure 11 shows the TEM photographs of these replicas. In the as-quenched specimens containing these elements, fine insoluble particles were observed in the grain boundaries and matrices.

X-ray diffraction measurements were undertaken for the as-quenched specimens containing these insoluble particles. Figure 12 shows the results obtained. In the cases of the addition of Co and Ni, the insoluble particles were identified as BeCo and BeNi, respectively. In the case of Ti addition, the peaks with high intensity were observed, but they could not be identified precisely by the JCPDS card. However, the particle is considered to be the chemical compound of Be and Ti, such as $\text{Be}_{(10+n)}\text{Ti}_n$.

Figure 13 shows the evidence that such fine particles pin the advancing boundaries of the cells. This specimen was aged at 623 K for 1.2 ks. Arrow marks show the fine insoluble particles.

From the above facts, the main mechanism that the additives suppress the cell growth must be due to the pinning effect⁽³⁴⁾⁽³⁵⁾ of such particles. Moreover, the mobility (M) of the advancing boundary of the cell also will be decreased by the grain boundary segregation of these elements or such insoluble fine particles existing in the grain boundaries. These segregated elements and insoluble particles in the grain boundaries also must suppress the nucleation of the cell.

Finally, the reason why the hardening in the matrix was accelerated the addition of Co, Ni or Ti could not be

clarified in this study. The fine insoluble particles such as BeCo, BeNi and $\text{Be}_{(10+n)}\text{Ti}_n$, which exist in the as-quenched specimens, may have acted as the nucleation sites of the γ' phase on aging. However, it is considered that an excess addition of these elements may coarsen the insoluble particles and decrease the number of the nucleation sites of the γ' phase. As a result, a suitable amount of the additions must be indispensable for accelerating the start of the hardening, as shown in Figs. 5–7.

IV. Conclusions

The effects of the additions of 0.1–2.0% of Co, Ni and Ti on the cellular precipitation in a Cu–2%Be alloy on aging at 623 K after quenching from 1093 K were investigated by the quantitative metallographic method. The results obtained are as follows:

(1) The additions of Co, Ni and Ti hastened the hardening (precipitation of γ' phase) in the matrix and increased slightly the maximum hardness.

(2) The additions of Co, Ni and Ti refined the grain size of the as-quenched specimens and suppressed the cell growth on aging at 623 K. The quantitative correlation was found out between the effect of these elements on the grain growth in the Cu–2%Be alloy at 1093 K and that on the cell growth at 623 K.

(3) In the as-quenched specimens containing Co, Ni, and Ti, fine insoluble particles were observed. These particles were identified as BeCo, BeNi and $\text{Be}_{(10+n)}\text{Ti}_n$ by X-ray analysis. Therefore, it is considered that these particles suppressed the nucleation and growth of the cell.

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Fig. 13 TEM micrograph of Cu–2%Be–0.3%Co alloy aged at 623 K for 1.2 ks showing fine particles (BeCo) denoted by arrow marks pinning the migration of the advancing boundary of a cell.

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