Influence of Rapid Solidification on the Aging of a Cu-2.1 mass % Be-0.2 mass % Co Alloy*

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The influence of rapid solidification on aging of a Cu-2.1 mass % Be-0.2 mass % Co alloy has been investigated by means of hardness tests, X-ray diffraction and electron microscope observation. Rapid solidification (R.S.) induces small maximum hardness and prolongs the time to attain the maximum hardness in contrast to our former results on Cu-Ti and Ni-Ti alloys. The dominant factor of age-hardening of the R.S. alloy is dispersion of fine γ phase particles instead of coherent γ' phase in the commercially produced (C.P.) alloy. Transformation modes are about one for the R.S. alloy and about two for the C.P. alloy. The isothermal transformation rate of the R.S. alloy is lower than that of the C.P. alloy below 750 K. This difference is explained by preferential fine precipitation of γ phase instead of γ' phase. The isothermal transformation rate of the R.S. alloy is higher than that of the C.P. alloy at aging temperatures above 750 K. This result is in good agreement with our former results on Cu-Ti and Ni-Ti alloys.

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I. Introduction

Several experimental investigations for the phase decompositions of Cu-Ti⁽¹⁾ and Ni-Ti⁽²⁾ alloys have been previously performed. The mechanical properties are improved and the energy for alloy production is considerably saved by rapid solidification. Rapid solidification increases the solubility ranges of the alloys and the kinetic constants of transformations in contrast to other results on Al-Zn⁽³⁾ and Fe-Mo⁽⁴⁾ alloys.

Aging behavior of Cu-Be alloys⁽⁵⁾⁻⁽¹⁰⁾ has been investigated by many workers because of their marverous and complex age-hardening. During aging, G.P. zone, γ' phase and γ phase precipitate in grains and γ phase on grain boundaries. Co atom prevents the precipitation at grain boundaries⁽¹⁰⁾ and improves the mechanical properties of the alloy.

The purpose of the present work is to investigate the influence of rapid solidification on decomposition kinetics of supersaturated Cu-2.1 mass % Be-0.2 mass % Co alloys.

II. Experimental Procedures

Cu-2.1 mass % Be-0.2 mass % Co alloys commercially used were melted in argon gas by infrared heating and rapidly solidified using a piston-anvil quenching apparatus shown in Fig. 1. Foils obtained about $250 \pm 50 \mu\text{m}$ in thickness were verified to be crystalline supersaturated solid solution, by means of X-ray and electron diffraction. Aging was performed for various durations in an argon electric furnace for prolonged aging and in a salt bath for short time aging. The decomposition procedures were investigated by means of micro-Vickers' hardness tests (Lood, 2.94 N), X-ray diffraction and electron microscope observation.

Fig. 1 Rapid solidification apparatus

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III. Results and Discussion

1. The influence of cooling conditions

Cooling conditions were varied by changing the thickness of the foils. Figure 2 shows a relation between the hardness and the thickness of the foils. The hardness is almost constant ($H_v = 160 \pm 30$) between 50 and 300 μm in thickness. The hardness of the R.S. alloy is larger than that of the C.P. alloy ($H_v = 105$, Fig. 3). This might be caused by introduction of the grain boundaries, excess lattice defects and fluctuation of solute concentration by rapid solidification. Photograph 1-(c) shows the columnar structure

Fig. 2 Hardness changes in rapidly solidified Cu-2.1 mass% Be-0.2 mass% Co alloy as a function of thickness which indicates the cooling condition.

Fig. 3 Hardness changes in commercially produced (C.P.) (a) and rapidly solidified (R.S.) (b) Cu-2.1 mass% Be-0.2 mass% Co alloys as a function of time at various aging temperatures.

perpendicular to the grown direction taken by a scanning electron microscope. The grain size of R.S. alloy (the diameter of columnar structure) is fine (about 2 μm) and is one tenth as small as that of the C.P. alloy (about 25 μm , Photo. 1-(a)). The etching amount of the interface of the columnar structure is larger than that of the grain boundary of the C.P. alloy (Photo. 1-(a)). This increase might be induced by excess defects introduced by rapid solidification. The half width value (V.H.W.) before aging of the R.S. alloys (Fig. 4) is wider than that of the C.P. alloy possibly because of excess defects introduced by rapid solidification. This results indicate that there are a great number of lattice defects in the R.S. alloy. Furthermore, many diffused islets (about 0.05 μm in diameter) are observed in a bright field transmission electron micrograph of the quenched foil, although an electron diffraction pattern (220) taken from the same area shows only main spots from the matrix lattice (Photo. 2) and the lattice constant is equal to that of the C.P. alloy before aging (Fig. 4). This result shows that the Cu-2.1 mass% Be-0.2 mass% Co alloy rapidly solidified is solid solution in which the fluctuation of solute concentration exists slightly. From these results we conclude that the increase in measured hardness of R.S. alloy might be induced by these islets, fine grains and excess defects introduced during rapid solidification.

2. Age-hardening

The maximum hardness of the R.S. Cu-2.1 mass% Be-0.2 mass% Co alloy is less than that of the commercially produced (C.P.) one at all temperatures investigated (Fig. 3). The aging time to attain the maximum hardness of the R.S. alloy is longer than that of the C.P. one (Fig. 3) in contrast to the previous results on Cu-Ti⁽¹⁾ and Ni-Ti⁽²⁾ alloys.

The lattice parameter of the matrix (Fig. 4) is an indicator of Be concentration in the matrix. The concentration of Be decreases to the solubility limit during aging. The precipitated phases were investigated to discuss the phase transformation in detail. Precipitation of γ' ($a = 2.79 \times 10^{-10}$ m, $c = 2.54 \times 10^{-10}$ m) and γ ($a = 2.572 \times 10^{-10}$ m) phases was confirmed by

Photo. 1 Scanning electron micrograph of commercially produced ((a), (b)) and rapidly solidified ((c), (d)) Cu-2.1 mass% Be-0.2 mass% Co alloys. (a) and (c) are before aging. (b) and (d) are after aging at 623 K for 3.6 ks.

Fig. 4 Changes in hardness, lattice spacing and value of half width for C.P. and R.S. Cu-2.1 mass% Be-0.2 mass% Co alloys as a function of aging time.

X-ray diffraction as shown in Fig. 5. The relative intensity of diffraction from the γ' phase is weaker in the R.S. alloy than that in the C.P. alloy. The intensity of diffraction from the γ phase is stronger in the R.S. alloy. These results show that the rapid solidification changes the ratio of the precipitated volume of the γ' to that of the γ phase.

Generally, a dominant factor of age-hardening of the C.P. Cu-Be alloy is the precipitation of γ' phase. This precipitation induces coherency between the γ' and the matrix and increases the V.H.W. of matrix (Fig. 4). However, the increasing rate of V.H.W. of the R.S. matrix is smaller than that of the C.P. alloy during aging. This means that the precipitation rate of γ' in the R.S. alloy is smaller than that in the C.P. alloy. The maximum V.H.W. of the R.S. alloy is approximately a half of that of the C.P.

Photo. 2 Transmission electron micrograph and diffraction pattern of the rapidly solidified Cu-2.1 mass%Be-0.2 mass%Co alloy before aging.

alloy, indicating that the amount of γ' phase is smaller in the R.S. alloy than that in the C.P. alloy.

The hardness decreases when coarse γ phase particles precipitate (Photo. 1-(b)) at grain boundaries in the C.P. alloy. Fine white particles precipitate in the R.S. alloy after aging at 623 K for 3.6 ks (Photo. 1-(d)) and increase the hardness. These results show that a dominant factor of age-hardening of the R.S. alloy is mainly the dispersion of the fine γ phase particles in contrast to the precipitation of γ' phase in the C.P. alloy.

3. Kinetic analysis

Rapid solidification decreases γ' phase and increases fine γ phase in the Cu-2.1 mass% Be-0.2 mass% Co alloy during aging. We try to discuss the kinetic form of precipitation of γ' and γ phase.

Fig. 5 Relative intensity of X-ray diffraction (I/I_m) for C.P. and R.S. Cu-2.1 mass% Be-0.2 mass% Co alloys on aging for 3.6 ks at 623 K. I is the intensity of γ and γ' phase. I_m is the intensity of matrix (200). The value of half width of γ phase of R.S. alloy is larger than that of C.P. alloy.

Johnson and Mehl⁽¹¹⁾ have proposed a quantitative method of kinetic analysis of the phase transformation. Their equation is

$$X = 1 - \exp(-(kt)^n), \quad (1)$$

and is modulated to

$$\log(-\ln(1-X)) = n(\log t + \log k), \quad (2)$$

where X is the transformed volume fraction, k is a kinetic constant, t is the time of aging and the exponent n is determined by the transformation mode. The fraction X is estimated from the hardness change ($X=0$ before aging and $X=1$ at the maximum hardness). The parameters k and n are determined by plotting $\log(-\ln(1-X))$ versus $\log t$ as shown in Fig. 6 and summarized in Table 1. It can be known that the transformation modes during aging at temperatures between 623 and 723 K are about one for the R.S. alloy and about two for the C.P. alloy. From these transformation modes we conclude that a certain number of γ' nuclei precipitate with two dimensional growth in the C.P. alloy and a certain number of γ nuclei precipitate with one dimensional growth in the R.S. alloy⁽¹²⁾. Precipitation of γ' thin plate was observed by means of transmission electron microscopy⁽¹³⁾, showing two dimensional

Fig. 6 Relation between $\log(-\ln(1-X))$ and $\log t$ for C.P. and R.S. Cu-2.1 mass% Be-0.2 mass% Co alloys at various aging temperatures.

Table 1 Transformation mode (n) and kinetic constant (k) for C.P. and R.S. Cu-2.1 mass% Be-0.2 mass% Co alloys at various temperatures.

Aging temperature /K	R.S. n	process k	C.P. n	process k
623	1.02	2.19×10^{-3}	1.78	1.81×10^{-3}
673	0.86	3.40×10^{-3}	2.10	2.03×10^{-3}
723	1.00	4.50×10^{-3}	1.92	2.97×10^{-3}
773	0.88	5.68×10^{-3}	1.56	2.86×10^{-3}
823	—	—	1.68	4.37×10^{-3}

growth of γ' . The white γ phase particles grow as shown in Photo. 1-(d). Though we cannot clearly know the shape of γ phase, we may conclude that the γ phase particles do not grow to thin plate but may grow to particles.

4. Isothermal transformation curves

Isothermal transformation curves can be derived from hardness changes, as shown in Fig. 7. The precipitation mechanism of the C.P. alloy in the temperature range from 623 to

Fig. 7 Isothermal transformation curves for C.P. and R.S. Cu-2.1 mass% Be-0.2 mass% Co alloys.

723 K is known as follows⁽⁷⁾:

Supersaturated solid solution $\rightarrow \gamma'$ phase $\rightarrow \gamma$ phase. However, rapid solidification decreases γ' phase and increases γ phase. Preferential precipitation of γ phase can be explained by taking into account of the effects of grain boundaries and excess lattice defects introduced by rapid solidification. These increase precipitation sites of γ phase particles. Especially excess lattice defects increase the rate of γ to γ' phase transformation and traps Co atoms, which prevents the mobility of Be to grain boundaries. We conclude that the decrease in the rate of precipitation during aging at lower temperatures depends on the change in precipitation form induced by rapid solidification.

Above 773 K the rate of γ phase precipitation is larger in the R.S. alloy than that in the C.P. alloy during aging. The aging time to attain $X=0.2$ for the R.S. alloy is only $10^{-0.8}$ of that for the C.P. alloy. This result, approximately, corresponds to the effect of rapid solidification ($10^{-1.2 \pm 0.2}$) on aging of the Cu-Ti alloy⁽¹⁾ in which precipitation is independent on the processes of alloy production. Excess lattice defects, which are indicated by the V.H.W. of matrix before aging as shown in Fig. 4, increase the rate of precipitation of the γ phase. From these results we conclude that rapid solidification increases the rate of precipitation, when it does not change the form of transformation.

IV. Conclusion

Cu-2.1 mass% Be-0.2 mass% Co alloys were

directly produced by rapid-solidification and then aged. Rapid solidification induces smaller maximum hardness and longer time to attain the maximum hardness, contrary to our previous results on Cu-Ti⁽¹⁾ and Ni-Ti⁽²⁾ alloys. The dominant factor for age-hardening of the R.S. alloy is dispersion of fine γ phase particles instead of precipitation of γ' phase in the C.P. alloy. Transformation modes are about one in the R.S. alloy and about two in the C.P. alloy. The rate of isothermal transformation of the R.S. alloy is lower than that of the C.P. alloy below 723 K. These phenomena are attributed to the preferential fine precipitation of γ phase instead of γ' phase. The rate of γ phase precipitation of the R.S. alloy is higher than that of the C.P. alloy at all over the temperature ranges. This result is in good agreement with previous results on the Cu-Ti⁽¹⁾ and Ni-Ti⁽²⁾ alloys.

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