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Liquid separation behavior of Cu-Co alloy during isothermal process at high temperature ①

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[Abstract] Liquid separation of Cu75Co25 and Cu85Co15 alloys at various supercoolings was investigated employing glass flux technology. The results reveal that during the course of isothermal processes, liquid separation develops more fully than in the continuous cooling, which results in more and larger particles. Further thermodynamic analyses indicate that primary dendrites from liquid separation are inclined to remelt in Cu liquid and finally the dendrites shrink locally, or even break into fragments. The fragments clash each other and grow into larger Co-rich particles due to electromagnetic force. It is also showed that at constant temperature whether Co-rich particles solidify depends on the develop level of the liquid separations. Co-rich liquid droplets begin to solidify when the component of Co-rich liquid reaches the solidus.

[Key words] Cu-Co alloys; liquid separation; supercooling; solidification
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1 INTRODUCTION

In 1958 Nakagawa found that there exits a metastable miscibility gap (MG) in Cu-Co alloys. That is, when Cu-Co alloy is supercooled to MG, two liquid phases, namely Co-rich phase and Cu-rich phase will form[1]. This unexpected phase transformation wil cause the inhomogeneous microstructure under the condition of mass loss and supercooling[2]. Especially liquid separation may take place during melt-spun process, which will cause solution atoms to segregate, and Co-rich phase with large size may reduce giant magnetoresistance (GMR) greatly[3]. In order to solve these problems, detailed investigations were carried out[3~10]. But there were no related reports on the whole course of liquid separation. What's more, before the liquid alloy reaches MG line, α-Co dendrites will inevitably form[3,5,6]. The changes at high temperature and the role on liquid separation have not been reported. This paper covers the impacts of isothermal process within MG zone on liquid separation of Cu-Co alloys with high Co content.

2 EXPERIMENTAL

High-purity copper (99.95%) and high-purity cobalt (99.9%) were used to prepare Cu-Co alloys. The starting materials with the designed compositions were arc melted employing a non-consumable tungsten electrode. In order to obtain homogeneous samples, several remelting cycles were performed, and the ingots were turned upside down before each remelting. Subsequently, the ingots with a mass of 8.5 g together with special glass (70% Na_2SiO_3 + 12.27% B_2O_3 + 17.73% $Na_2B_4O_7$) were inserted into quartz tube filled with Ar gas. After they were heated to 1 920 K using high frequency induction, the electric power was switched off in order to cool the samples freely. When the temperature was below the target temperature, appropriate output was applied in order to keep the temperature constant. The cooling curves of samples were recorded by infrared temperature measuring meter WHF-655 and X-Y recorder. At a certain temperature, recalescence occurred in Co-rich liquid. Once the clear exothermal peak was measured, switch off the power and let the samples cool freely. The time span from the beginning of isothermal process to the occurring of recalescence was marked as Δt. When ingots completely solidified, they were quenched into water to prevent the solid phase transformation. The ingots were cut, polished and etched with 25% NH_3 solution for optical microscopy examination. (Mex-3). The compositions of phases were examined using AMRAY-1000B SEM equipped with energy dispersive spectroscopy (EDS).

3 RESULTS

3.1 Cooling curves

Typical cooling curves of Cu75Co25 and Cu85Co15 alloys are shown in Fig. 1. These curves are characterized by two inflexion points above the isothermal temperature. Based on phase diagram and microstructure analyses, one inflexion point, marked

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as T_d, is related to the precipitation of primary dendrites; the other point, marked as T_s, responds to the beginning of liquid separation.

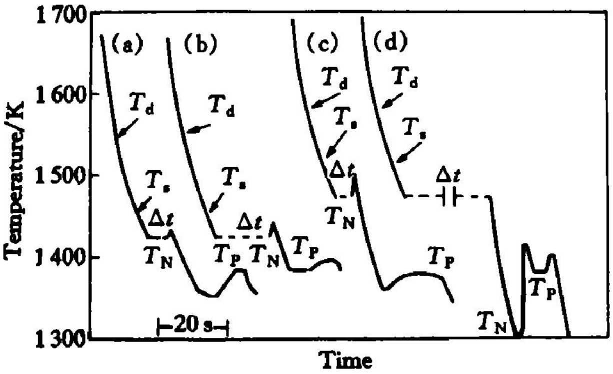

Fig. 1 Cooling curves of Cu-Co alloys with isothermal process

When the samples are kept at constant temperature for Δt, a clear exothermic peak appears, as shown in Fig. 1(a), (b) and (c). According to the Refs. [5~ 7], the exothermic peak results from the solidification of Co-rich liquid. If power is switched off, the exothermal phenomena is detected during the course of cooling (as shown in Fig. 1(d)), which results from the solidification of Co-rich liquid. There is another exothermal peak below the isothermal temperature, which is came from the solidification of residual Co-rich liquid.

3.2 Microstructures

Fig. 2(a) shows the microstructure of Cu85Co15 alloy that is processed isothermally at 1 423 K. It can be seen that there are two shapes of Co-rich phases embedded in Cu matrix: one is α-Co dendrites formed at small supercooling; the other is spherical Co-rich phase produced from liquid separation at large supercooling. Further analysis indicates that part of the spherical Co-rich particles grow directly within the melt; part of them are interspersed with dendrites, which indicates the growth manner is heterogeneity nucleation. In any case, dendrites-free zone can be observed around the Co-rich particles. The results suggest that Co-rich particles can enclose the dendrites nearby and make them attach to the particles when they grow. For example, when isothermal temperature is 1 473 K and the time span (Δt) is 3 s, the microstructure characteristics of Cu75Co25 alloy after solidification are roughly in accordance with those of Cu85Co15 alloy. The only difference is the amount of Co-rich particles and α-Co dendrites because of deferent Co contents, as shown in Fig. 2(b).

Isothermal process ensure that the liquid separation is developed fully in time. When holding time is

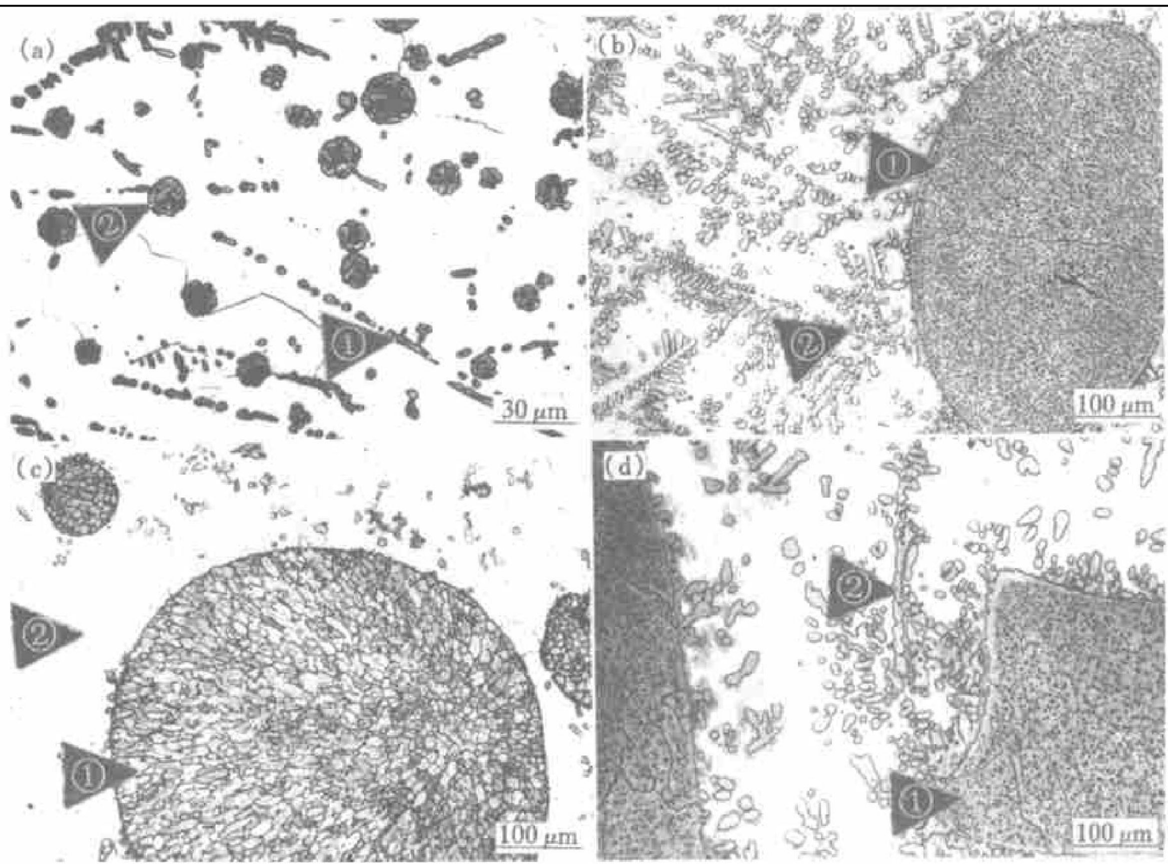

Fig. 2 Microstructures of Cu-Co alloys
(Isothermal temperature is 1 423 K for Cu85Co15 and 1473K for Cu75Co25)
(a) —Cu85Co15, Δt = 5 s (Arrow: ① α-Co dendrite, ② Co-rich droplet);
(b) —Cu75Co25, Δt = 3 s (Arrow: ① Co-rich droplet, ② α-Co dendrite);
(c) —Cu85Co15, Δt = 15 s (Arrow: ① Co-rich particle, ② Cu-rich matrix);
(d) —Cu75Co25, Δt = 180 s (Arrow: ① Co-rich droplets, ② α-Co dendrite segment)

long enough, for Cu85Co15 alloy, the size of the maximal Co particle is more than 500 μm, as shown in Fig. 2(c). For Cu75Co25 alloy, the size of that is up to 1 mm, as shown in Fig. 2(d). At meantime, the amount of those Co particles with big size increases obviously. While the samples are eroded appropriately, it is found that those spherical Co-rich particles with big size consist of small irregular bar-like Co-rich particles or dendrite-like grains, as shown in Fig. 3. This indicates that dendrites can cluster together and form large Co particles. This result can not be acquired during continuous cooling process.

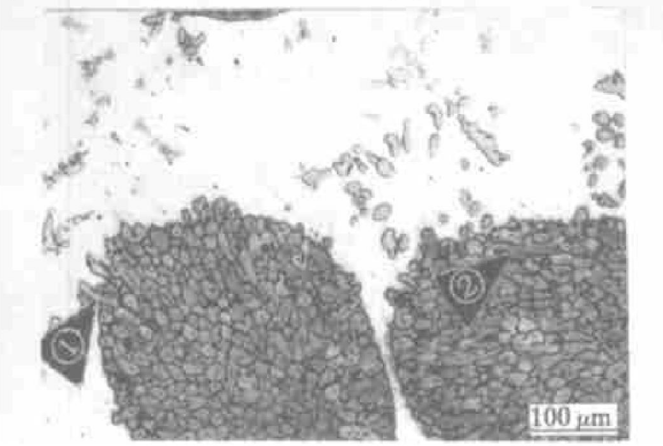

Fig. 3 Microstructure of Cu75Co25 alloy
(T = 1473 K, Δt = 180 s)
(Arrow ① and ②: α-Co dendrite segments)

3.3 Component of Co-rich particles

Energy dispersive spectroscopy (EDS) analysis results (as listed in Table 1) reveal that the component of dendrites is in accordance with the phase diagram. For Cu75Co25 alloy, Co content in Co-rich particles from liquid separation is 80.8% (mole fraction); for Cu85Co15, the Co content is 85.6%. The difference comes from the different isothermal temperature (the isothermal temperature of Cu85Co15 is more than that of Cu85Co15). For Cu75Co25 alloy, if Co-rich phase has not solidified during the isothermal process, the component of large Co-rich particles is lower than that on the liquid separation line.

4 DISCUSSION

When Cu-Co alloys are cooled down into liquid separation zone, there are three phase: Co-rich liquid, Cu-rich liquid and α-Co dendrites. The results indicate that α-Co dendrites are unstable and they are inclined to remelt into Cu liquid.

Based on the regular solution model, the mixed Gibbs energy in Cu-Co binary alloy system with liquid separation is as follows[5].

$$\Delta G_{\mathrm{L}} = \Omega x(\mathrm{Cu})x(\mathrm{Co}) + RT[x(\mathrm{Cu})\ln x(\mathrm{Cu}) + x(\mathrm{Co})\ln x(\mathrm{Co})] \quad (1)$$

where $x(\mathrm{Cu})$ and $x(\mathrm{Co})$ stand for the molar fraction of Cu and Co respectively, Ω is the interaction factor.

Within liquid separation zone, the interaction factor of liquid components is

$$\Omega(\mathrm{L}) = [2 - 1.05\times 10^{-3}(T - T_{\mathrm{P}})]RT_{\mathrm{mB}} \quad (2)$$

While on the solidus, the interaction factor of solid component $\Omega(\mathrm{S}) = 2RT_{\mathrm{mB}}$.

Gibbs free energy curves of metastable liquid and α-Co can be calculated from the above formula and are shown in Fig. 4. From the view of thermodynamics, there is a critical temperature, marked as T_{SC}. When the temperature is below T_{SC}, free energy of α-Co is less than that of metastable Co-rich liquid, as shown in Fig. 4(c). When the temperature is above T_{SC}, free energy of α-Co is larger than that of metastable Co-rich liquid, as shown in Fig. 4(a). In this case, there are two possible equilibrium states, namely α-Co and Cu-rich liquid, Cu-rich liquid and Co-rich liquid. But the latter has lower free energy than the former do. Therefore the dendrites from liquid separation are metastable and apt to remelt into Cu-rich liquid.

From the view of dynamics, primary dendrites remelt into Cu-rich liquid and dendrites shrink locally and even separated into fragments. Part of dendrites disappears. These accelerates the growth of Co-rich particles. This may explain the existence of dendrites-free zone. When they are heated by employing high frequency induction, electromagnetic force exits inevitably. Electromagnetic force accelerates the separation of dendrites and the aggregation and growth of Co-rich particles. During the course of growth, Co-rich particles enclose the dendrite fragments and they became part of Co-rich particles, as shown in Fig. 2(d).

From Fig. 4, it can be seen that the borderline of MG expands with the reduction of temperature. Therefore it can be inferred that under the condition of quick cooling the component of Co-rich and Cu-rich liquids deviates from that on the MG. When the com-

Table 1 Components of large Co-rich particles analyzed by EDS

Alloy	Isothermal temperature/K	Holding time/s	x(Co)/%	x(Cu)/%	Note
Cu75Co25	1473	10	80.8	19.2	Solidified during isothermal process
Cu85Co15	1423	10	85.6	14.4	Solidified during isothermal process
Cu75Co25*	1473	180	77.5	22.5	Solidified after isothermal process

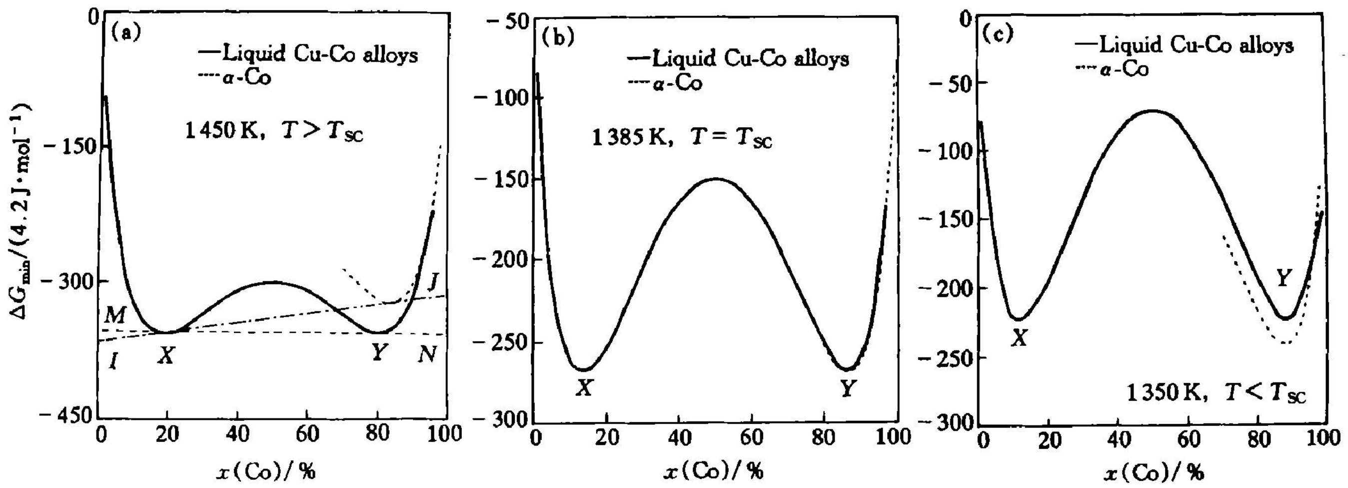

Fig. 4 Mixing Gibbs free energy curves of metastable liquid and α-Co phase in Cu-Co alloys

ponent of Co-rich liquid is located within MG and the temperature is lower than T_{SC}, it will not solidify unless the supercooling is large enough and mixing free energy of α-Co is less than that of Co-rich liquid. This result contrasts with Robinson's[9]. He thinks that alloys with different components have similar T_N.

When the component of Co-rich liquid is located within MG, liquid separation happens. On the contrary, Co-rich liquid is in equilibrium. Therefore the borderline of MG also indicates that of equilibrium and metastable equilibrium phase transformation. Also supercooling is related to the component. At certain temperature, supercooling increases with Co content. When the temperature is above T_{SC} and Co content reaches MG, maximal supercooling can be obtained. Co-rich liquid solidifies regularly. Therefore whether Co-rich drops from liquid separation solidify depends on the extent of liquid separation. When Co content of Co-rich liquid does not reach MG, Co-rich liquid does not solidify until larger drive force at lower temperature is obtained. Liquid separation is typical diffusion transformation. It takes time for Co-rich drops to form at high temperature from liquid separation to reach MG. Isothermal process provides time condition. With time expanded or temperature fluctuated, the component of Co-rich liquid reaches MG and solidification occurs immediately. Therefore it can be interfered that during the course of quick supercooling, cooling speed impacts the extent of liquid separation.

5 CONCLUSION

1) Compared with continuous cooling, isothermal process will accelerate liquid separation, and larger and more particles will form.

2) During isothermal process, high temperature or small supercooling leads to remelting of primary dendrites. The fragments from dendrites promote the growth of particles because of electromagnetic force.

3) At constant temperature whether Co-rich particles solidify depends on the extent of the liquid separations. Co-rich liquid droplets begin to solidify when the component of Co-rich liquid reaches the solidus.

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