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Effects of Ni addition on liquid phase separation and giant magnetoresistance of Cu-Co alloys ①

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[Abstract] The effects of Ni addition on the liquid phase separation and giant magnetoresistance (GMR) of Cu-Co alloys were discussed. The results reveal that Ni addition can partially restrain the liquid phase separation of Cu-Co alloys, resulting in a decrease of volume fraction for the Co-rich particles separated from the liquid phase and in refined microstructures. The composition analyses indicate that Ni is dissolved in both the Co-rich and the Cu-rich phases, but Ni content in the Co-rich phase is much higher than that in the Cu matrix. At the same time, Ni addition enhance the solubility between Cu and Co, especially Cu in Co solid solution. Ni alloying into Cu-Co alloys can fully prevent the liquid phase separation during melt spinning, which is very beneficial to improve GMR of Cu-Co alloys.

[Key words] Cu-Co-Ni alloys; supercooling; melt-spun; liquid phase separation; microstructure; GMR
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1 INTRODUCTION

The liquid phase separation of alloys ($L \rightarrow L1 + L2$) is an especial phase transformation phenomenon under deep supercooling condition, which mainly occurs in the alloy systems with large, positive mixing heat, such as Cu-Co and Cu-Fe binary systems. The liquid phase separation of Cu-Co alloys was first revealed by Nakagawa in 1958[1]. Recently, it has been studied in detail because of the discovery of giant magnetoresistance (GMR) in melt-spun Cu-Co alloys[2] and the development of deep supercooling technologies such as free contain, fluxing and other techniques[3~8]. The metastable miscibility gap (MG) was also obtained by thermodynamic calculation and concentration measurement of liquid phase separation product[3,6]. But the effects of alloying on liquid phase separation of Cu-Co alloys and the investigation of liquid phase separation in ternary alloy systems were rarely reported.

The research results of GMR show that the higher supersaturation level of melt-spun Cu-Co alloy is more favorable to control the particle size and the density of small precipitation during annealing, and therefore larger GMR performances can be attained expectantly[9]. Unfortunately it is found that the liquid phase separation of Cu-Co alloys occurs inevitably during quick solidification when Co content is 10% ~ 50% (mole fraction)[10]. This undesired liquid separation results in very large Co-rich particles, limits the supersaturation level and then weakens GMR performance. Recent investigations[11,12] indicated that Ni addition could effectively improve GMR performance of Cu-Co alloys. In this article, the effects of Ni addition on liquid phase separation and the mechanism of enhancing GMR properties are discussed.

2 EXPERIMENTAL

High-purity copper (99.95%), cobalt (99.9%) and nickel (99.95%) were used to prepare Cu-Co-Ni alloys. The raw 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 a 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. The cooling curves of the samples were recorded by an infrared temperature measuring meter WHF-655 and X-Y recorder. When the ingots were completely solidified, they were quenched into water. The ingots were cut, polished and etched with a 25% NH_3 solution for optical microscopy examination. The composition of phases were examined using an AMRAY-1000B SEM equipped with energy dispersive spectroscopy (EDS).

The melt-spun ribbons of Cu-Co and Cu-Co-Ni alloys approximately 3 ~ 3.5 mm wide and 30 μm thick were produced by melt-spinning from silica cru-

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cibles onto a copper wheel under Ar gas pressure of 5×10^4 Pa. Measurements of the magnetoresistance (MR) of the ribbons were conducted by means of four-point method with the magnetic field ranging from 0 to 1.3T at the ambient temperature. The structure of met-spun Cu-Co and Cu-Co-Ni alloy ribbons were observed using H-800 Transmission Electron Microscopy (TEM).

3 RESULTS AND DISCUSSION

Fig.1 illustrates the continuous cooling curves of Cu80Co20 and Cu-Co-Ni alloys. It can be seen that there exists one inflexion point (denoted as T_S) on each curve. Microstructure characteristics shows that these inflexion points are related to the beginning temperature of liquid phase separation. When the temperature is below T_S, one thermal arrest (denoted as T_P) and two exothermal peaks were detected on each cooling curve. Microstructure analyses reveal that these arrests result from the peritectic reaction. The exothermal peaks between T_S and T_P result from the solidification of the Co-rich liquid from liquid phase separation. For convenience, the peak top and bottom temperatures are denoted as T_R and T_N respectively. The other exothermal peaks appeared after the peritectic reaction are responsible for the solidification of the remnant Cu-rich liquid.

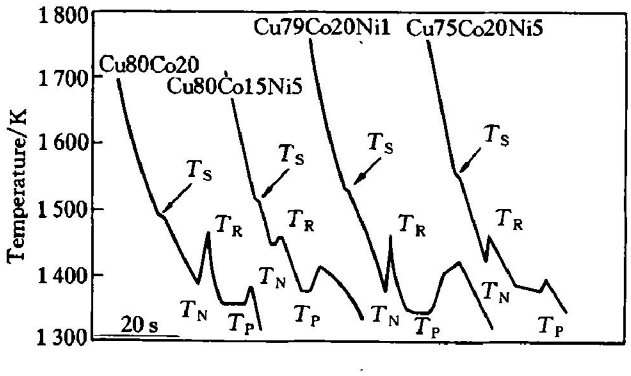

Fig.1 Cooling curves of Cu-Co and Cu-Co-Ni alloys under deep supercooling

From Fig.1, it is known that the morphology of cooling curves are not obviously changed by Ni addition. But Ni addition can shift T_S to higher temperature. At the same time, more Ni content produces the lower exothermal peak ($T_R - T_N$). Investigations[6,7] show that T_N descends with the increase of Co content in Cu-Co alloys. In this experiment it is found that Ni addition can increase T_N. For instance the T_N of Cu75Co20Ni5 alloy is 1430 K which equals to that of Cu90Co10 alloy. So increasing Ni content could be equivalent to decreasing Co content for liquid phase separation, and roughly adding 1% Ni will be equal to decreasing 2% Co. The exothermal peak results from the solidification of the Co-rich droplets, hence the decrease of exothermal peak amplitude means that the volume fraction of the Co-rich droplets is reduced by Ni addition.

Fig.2(a) shows the typical microstructure of finally solidified Cu80Co20 alloy. The diameter of some spherical Co-rich particles reaches 45 μm. When Ni content is only 1% (mass fraction), two shapes of Co-rich particles are found with refined microstructure. The maximal diameter of the spherical Co-rich particles from liquid phase separation is not larger than 20 μm, as shown in Fig.2(b). The size of the Co-rich particles from liquid phase separation, as shown in Fig.2(c), can be further decreased down to 5 μm when more Ni element is added to Cu-Co alloy. It is also noticed in Fig.2(c) that the microstructure is almost free of dendrites, which suggests that Ni addition can also restrain the formation of the dendrites. For Cu80Co15Ni5 alloy, a few dendrites and very fine Co-rich particles from liquid separation can be observed in Fig.2(d).

Table 1 lists the compositions of every phase for Cu-Co-Ni and Cu-Co alloys quantitatively analyzed by EDS. It is obviously found that Ni dissolves in both the Cu matrix and the Co-rich particles. But Ni quantity dissolved in Co-rich phase is much more than that in Cu-rich phase. It is also noticed that the Ni addition increases the intersolubility between Co and Cu, especially the solubility of Cu in Co. No new phase is detected in the samples.

The above results show that the Ni addition into Cu-Co alloys can partially restrain the liquid phase separation of Cu-Co alloys, resulting in the increase of the Co contents in Cu-rich matrix, and the decrease of the volume fraction and the size of the Co-rich particles from liquid phase separation.

The liquid phase separation zone of ternary Cu-Co-Ni system is calculated by the thermodynamic method, the projections of isothermal section (dash lines) are illustrated in Fig.3. The Cu-Ni binary system is completely soluble throughout the entire composition range. Co-Ni is approximate ideal system either in liquid or solid state[13]. Ni addition can decrease the mixing heat of Cu-Co alloys, resulting in the decline of driving force of liquid phase separation, which means the liquid phase separation needs a larger supercooling in Co-Co-Ni alloy compared with Cu-Co alloy. The intersolubilities of Cu and Co are increased by Ni addition, which means the miscibility gap boundaries approach each other. Fig.3 also shows the measurement compositions of phases from liquid phase separation. It is calculated that the mass fraction of Co-rich particles from liquid phase separation is 17% for Cu80Co20 alloy. If replace 5% Co by Ni (Cu80Co15Ni5 alloy), the mass fraction of Co-rich particles from liquid phase separation is only 7.5%.

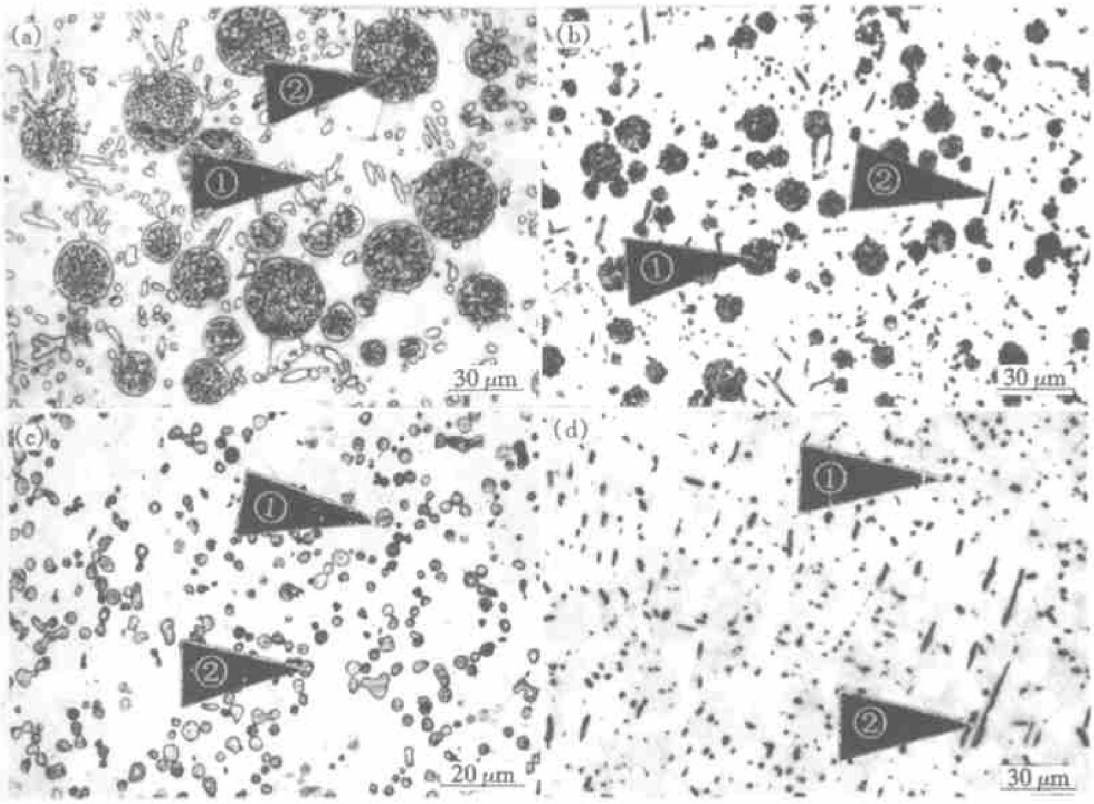

Fig. 2 Microstructures of Cu-Co and Cu-Co-Ni alloys
(a)—Cu80Co20 (Arrow: ① Dendrite, ② Co-rich droplet from liquid separation);
(b)—Cu79Co20Ni1 (Arrow: ① Co-rich particle from liquid separation, ② Dendrite);
(c)—Cu75Co20Ni5 (Arrow: ① Co-rich particle from liquid separation, ② Cu-rich phase in center of Co-rich particle);
(d)—Cu80Co15Ni5 (Arrow: ① Co-rich particle from liquid separation, ② Dendrite)

Table 1 Phase compositions of Cu-Co and Cu-Co-Ni alloys under deep supercoolings

Alloys	Liquid separation Co-rich phase			α-Co dendrite			Cu-rich matrix		
	w(Cu)/%	w(Co)/%	w(Ni)/%	w(Cu)/%	w(Co)/%	w(Ni)/%	w(Cu)/%	w(Co)/%	w(Ni)/%
Cu80Co20	16.0	84.0	-	14.0	86.0	-	92.2	7.80	-
Cu79Co20Ni1	19.2	75.8	5.00	20.0	74.7	5.30	91.4	8.30	0.30
Cu75Co20Ni5①	30.0	59.0	11.0	-	-	-	82.3	13.2	4.50
Cu80Co15Ni5	32.5	55.0	12.5	33.0	54.4	12.6	86.7	8.54	4.76

No dendrite is observed for Cu75Co20Ni5 alloy

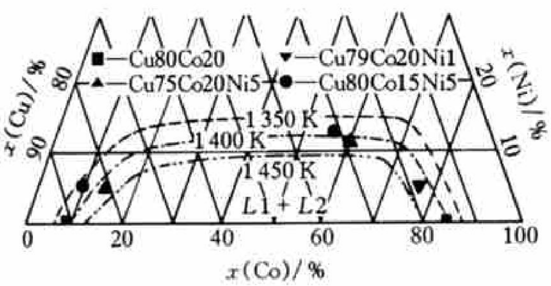

Fig. 3 Projections of ternary isothermal section of Cu-Co-Ni alloys
(Dash lines are calculated boundaries of isothermal section of liquid phase separation zone)

The prohibiting effects of Ni addition on the liquid separation are obvious.

The effects of Ni addition on restraining the liquid phase separation are proved again by microstructure analyses of melt-spun Cu-Co and Cu-Co-Ni alloys. Fig. 4 is the fine microstructures of melt-spun Cu80Co20 and Cu80Co15Ni5 alloys analyzed by TEM. For melt-spun Cu85Co15 alloy, spherical Co-rich particles (denoted by arrow) can be observed to be embedded in Cu-rich matrix. According to Ref. [10] and analysis of this paper, these large incoherent Co-rich particles are resulted from liquid phase separation during melt spinning. For melt-spun Cu80Co15Ni5 alloy, large incoherent Co-rich particles nearly disappear. The microstructure of the alloy is fine modulation structure, which means Ni addition can fully prevent the liquid phase separation during melt spinning.

Fig. 5 shows the effects of Ni addition on GMR performance of Cu-Co alloy. The experiments reveal that 5% Ni addition can enhance the GMR ratio of Cu85Co15 alloy from 5% to 7.2%. It is obvious that Ni addition can increase the supersaturation level of melt-spun solid solution, which is very beneficial to increase the density of small particles precipitated during annealing. Because Ni is a magnetic element, and its dissolving in the Co-rich phase can increase the fraction of magnetic phase and then enhance the GMR ratio.

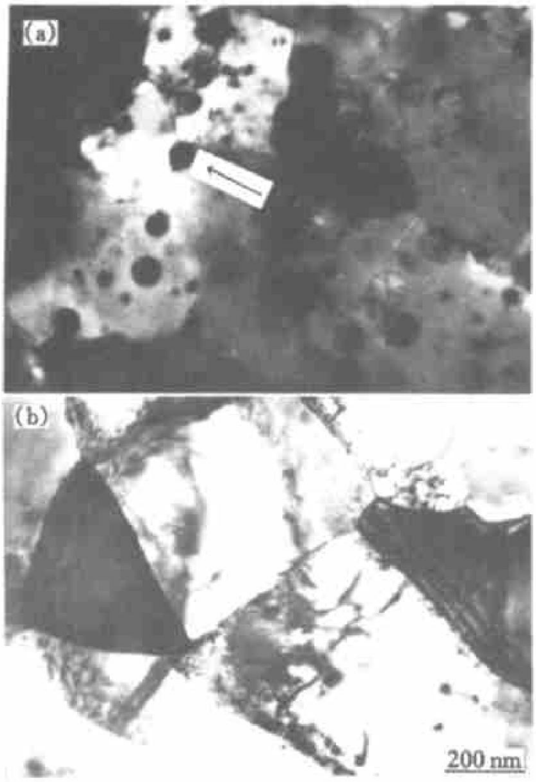

Fig. 4 TEM microstructures of melt-spun Cu80Co20 and Cu80Co15Ni5 alloys
(a)—Melt-spun Cu85Co15 alloy, as-quenched;
(b)—Melt-spun Cu80Co15Ni5 alloy, as-quenched

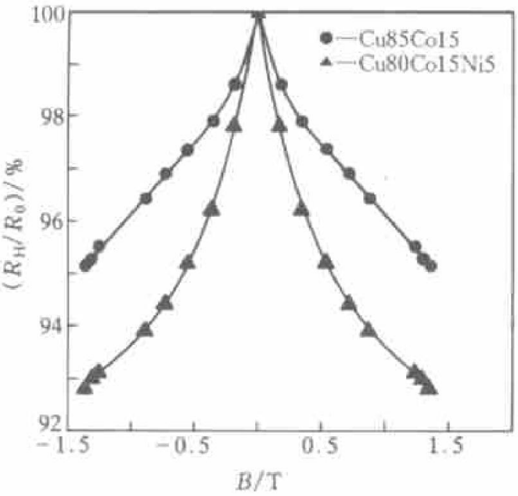

Fig. 5 Effects of alloying on GMR of Cu-Co alloys

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