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Microstructure and properties of Cu-15Ni-8Sn-0.4Si alloy①

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Abstract: By metallographic test, SEM, TEM and energy spectrum, the microstructure and properties of Cu-15Ni-8Sn-0.4Si alloy were studied. The results show that the added-Si combines with Ni and forms Ni_3Si and Ni_2Si phases. During ageing at 380 ℃, the precipitation of Ni_2Si phase suppresses discontinuous precipitation to some degree. After adding Si, the conductivity and hardness of Cu-15Ni-8Sn alloy are increased to some degree.

Key words: Cu-15Ni-8Sn-0.4Si alloy; spinodal decomposition; cast structure; discontinuous precipitation; Ni_2Si
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1 INTRODUCTION

Spinodal Cu-Ni-Sn alloys have been considered as substitutes for Cu-Be alloys because of low price, outstanding properties and so forth. It is a new Cu-base spring material with great potential[1-3]. In Cu-Ni-Sn system, Cu-15Ni-8Sn alloys are gradually stressed with high corrosion-resistance and excellent resistance to stress relaxation. However, there are few reports of this aspect in our country. It is very important to suppress the discontinuous precipitation for Cu-15Ni-8Sn alloy, at the same time, low conductivity should be compensated. Previous works have shown that the addition of Si in Cu-10Ni-8Sn alloy can retard discontinuous precipitation[4, 5]. Besides we have known that Ni and Si form compounds of Ni_3Si and Ni_2Si when Ni element is added in Si-bronze. Because of the precipitation of them, the alloy is strengthened after ageing and obtains good mechanical properties, corrosion-resistance, conductivity and so on[6]. It is indicated that properties of Cu-15Ni-8Sn alloy added Si are influenced by the formation of Ni_3Si and Ni_2Si phases. In this paper, the Cu-15Ni-8Sn alloy added 0.4% Si is considered. Starting at the cast structure of the alloy, the microstructure and properties are studied.

2 EXPERIMENTAL

The raw materials used were electrolytic copper, high-purity nickel, high-purity tin and silicon. Cu-15Ni-8Sn alloy (mass fraction, %) was prepared by melting the component metals in an intermediate frequency induction furnace. The ingot obtained (230 mm × 90 mm × 40 mm) was homogenized at 860 ℃ for 4h after its surface defects were cut off, then hot rolled at 860 - 650 ℃, and subsequently cold rolled by 84% after solution at 850 ℃ for 1h and shaped into a suitable form for the following measurements, yet before measuring, the specimens were aged at 380 ℃. Optical microscopy observation was taken on NEPHOT-21 instrument. SEM was performed on KYKY-2800 instrument followed by energy spectrum. Conductivity was measured by double bridge. Hardness was measured by model HMV-2T low load micro-Vickers hardness tester.

3 RESULTS

3.1 Analysis of cast structure

Fig. 1 shows the metallographs of cast structure of Cu-15Ni-8Sn-0.4Si alloy. We find that the treelike crystal of cast structure in Cu-15Ni-8Sn-0.4Si alloy is developed (Fig. 1(a)). The cast structure is classified into three layers: the grayish white treelike crystal with many particles whose density increases gradually from inside to outside; the black matter around the treelike crystal; and the brilliant white second-phase educts between treelike crystals. All these things are clearer in high power microscope (Fig. 1(b)). In order to analyze the cast structure of Cu-15Ni-8Sn-0.4Si alloy qualitatively, SEM and energy spectrum are taken.

Fig. 2 shows a group of stereoscan photograph in same field. It can be seen that its structure is similar with that of metallographs. In high power, stereoscan photograph shows different details from metallograph (Fig. 2(b)). It is represented that: 1) The thick black matter in metallograph (white field in stereoscan photograph) consists of many rodlike particles; 2) brilliant white educts in met-

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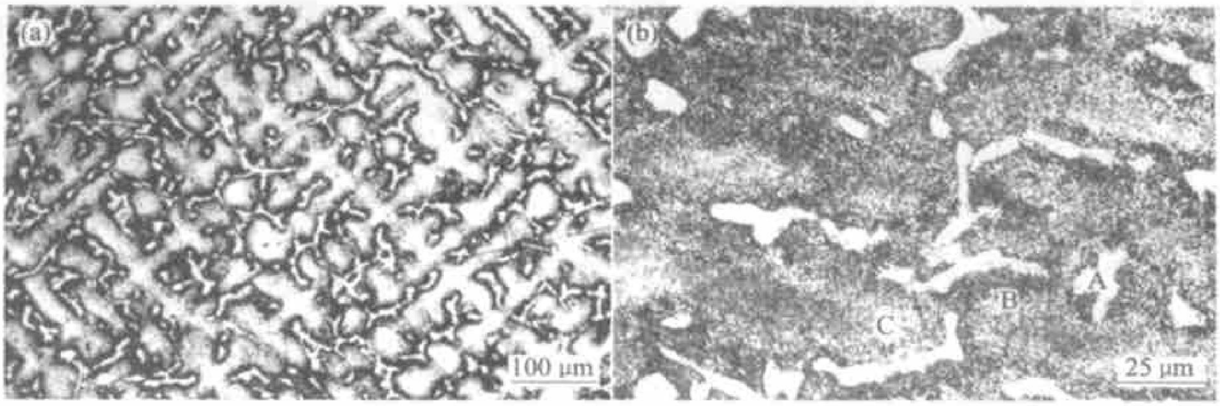

Fig. 1 Metallographs of cast structure of Cu-15Ni-8Sn-0.4Si alloy

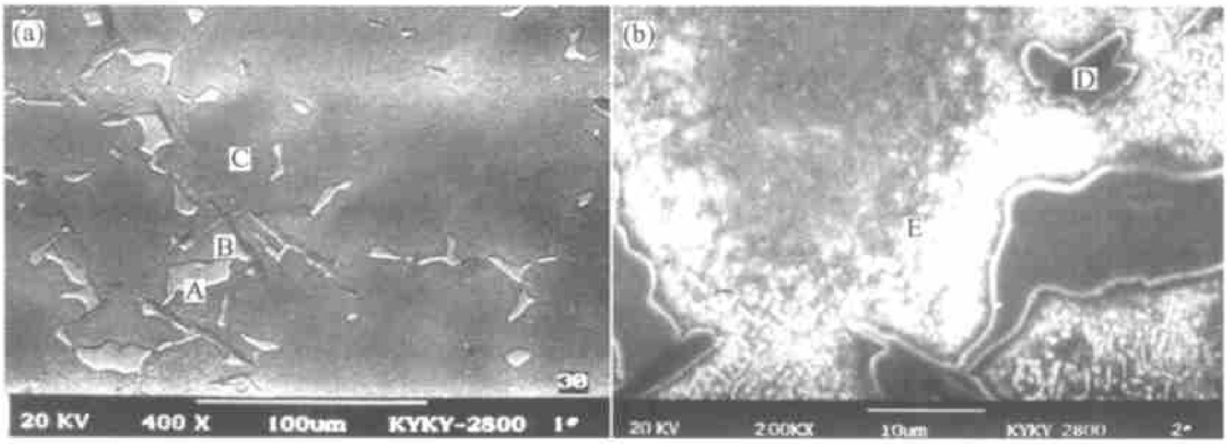

Fig. 2 Stereoscan photographs of cast structure of Cu-15Ni-8Sn-0.4Si alloy
(a) —Backscattered electron image; (b) —Secondary electron image

allograph (grayish white massive matter in stereoscan photograph) consists of two kinds of matters, of which one is light in color and the other is dark in color. In backscattered electron image (Fig. 2(a)), most massive second-phases are white. It is apparent that these brilliant white second-phases are concentrated phases of heavy metal (Sn), whose coefficient of atomic scattering is large. However, some of massive matters are black in reverse. This is the display of concentrated phases of light metal (Si).

The result of energy spectrum analysis in the cast structure of Cu-15Ni-8Sn-0.4Si alloy is listed in Table 1, in which, data of No. 1, 2 and 3 are micro-area chemical analyses of A, B and C spots in backscattered electron image. Namely, they are brilliant white educts, black matter and grayish white treelike crystal. Data of No. 4 and 5 are micro-area chemical analyses of D and E spots in secondary electron image. Namely, they are dark colored field on grayish white massive matter and white rodlike particles between grayish white treelike crystal and grayish white massive matter in Fig. 2 (b). It can be seen that atomic proportion of every element in grayish white massive matter is that the ratio of Cu: Ni: Sn: Si is 6.3: 6.1: 3.5: 1. Therefore, it is the $(Cu, Ni)_3Sn$ phase, possibly, there is the Ni_3Si phase in it[7]. Atomic proportion of every element in the dark colored field of grayish white massive matter is that the ratio of Cu: Ni: Si is equal to 1: 8.1: 4.7. It should be Ni_2Si phase soluting a few copper atoms[8]. The grayish white treelike crystal is the phase of lack Sn (1.25%, mass fraction). So, it is Cu-Ni solution with rich Ni (17.72%, mass fraction). The white field between treelike crystal and grayish white massive matter is a transitional field in which the content of Ni is lower than average, while the content of Sn is higher. Because its structure is complex, it can't be sure by energy spectrum analysis. The result of energy spectrum analysis is consistent with that of backscattered image.

In short, there is serious dendritic segregation of Sn element in the cast of Cu-15Ni-8Sn-0.4Si alloy. However, the distribution of Ni element is homogeneous basically without consideration of $(Cu, Ni)_3Sn$, Ni_3Si and Ni_2Si phases. Compared with ordinary Cu-Ni-Sn alloys, the addition of Si makes experimental alloy produce new phases of Ni_3Si and Ni_2Si.

3.2 Change of microstructure during aging

Fig. 3 shows metallographs of Cu-15Ni-8Sn alloys without Si and with 0.4% Si after ageing for 24

h. Fig. 4 shows TEM images of Ni_2Si phases in Cu-15Ni-8Sn alloy with 0.4% Si during ageing. It can be seen that after ageing at 380 ℃ for 24 h, Cu-15Ni-8Sn alloy without Si has already generated discontinuous precipitation. The discontinuous precipitate grows up and develops constantly from grain boundaries to intracrystalline. However, for Cu-15Ni-8Sn-0.4Si alloy, the Ni_2Si phase forms because the Si addition suppresses the nucleation and growth of discontinuous precipitate to some degree. With increasing ageing time, the Ni_2Si phase particles grow up and the suppressing effects are decreased. Ageing at 380 ℃ for 24 h, Cu-15Ni-8Sn-0.4Si alloy also generates discontinuous precipitation, which is slower than that of Cu-15Ni-8Sn alloy.

3.3 Analyses of properties

Fig. 5 shows the relationship between the aging time at 380 ℃ and the conductivity at room temperature. It can be seen that the conductivity is increasing with increasing time. At the beginning, it is increased quickly, and then becomes slower. Until ageing for 10 h, the conductivity is increased to 10.9% without decreasing tendency. As current-carrying component, the conductivity is very important. Be-bronze can reach 20% or so. It is reported that the conductivity of Cu-15Ni-8Sn alloy (cold rolled by 97%, aged at 400 ℃) is only

Table 1 Energy spectrum analysis of cast structure of Cu-15Ni-8Sn-0.4Si alloy

Number	Mass fraction/%				Mole fraction/%			
	Cu	Ni	Sn	Si	Cu	Ni	Sn	Si
1	33.41	30.03	34.22	2.34	37.32	36.31	20.47	5.90
2	76.71	12.12	10.26	0.91				
3	80.17	17.72	1.25	0.85				
4	9.47	70.87	0	19.66	7.25	58.71	0	34.04
5	75.79	12.38	10.59	1.24				

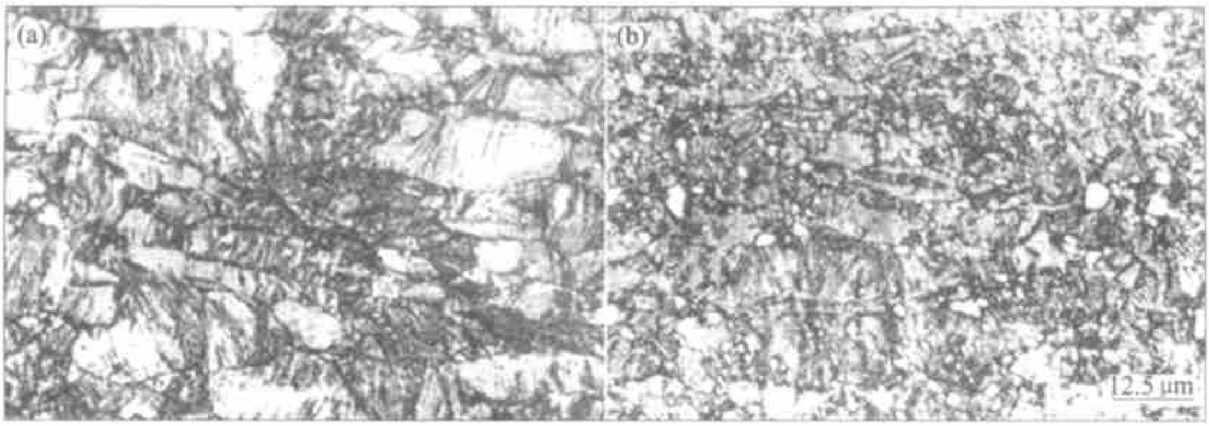

Fig. 3 Metallographs of two Cu-15Ni-8Sn alloys after ageing for 24 h
(a) —Si-free; (b) —0.4% Si

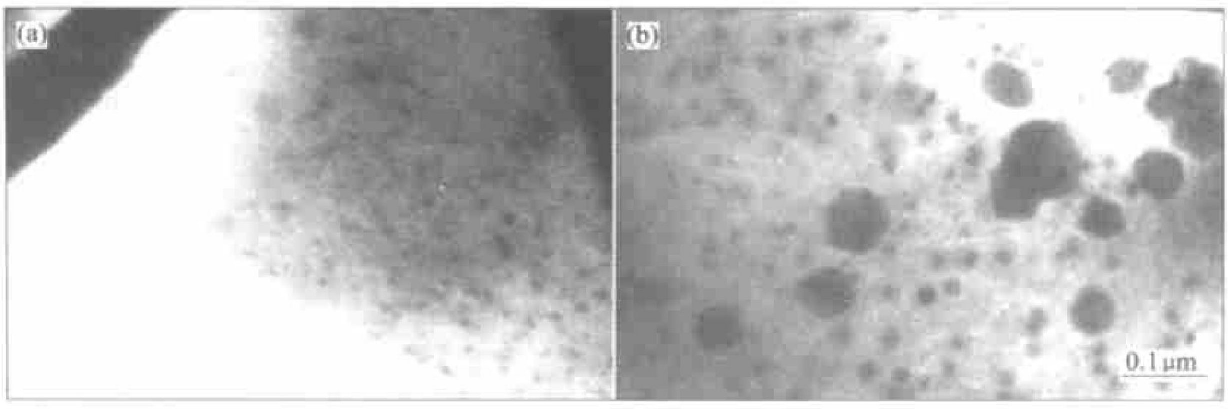

Fig. 4 TEM images of Ni_2Si phase of experimental alloy during ageing
(a) —Ageing for 0.5 h; (b) —Ageing for 24 h

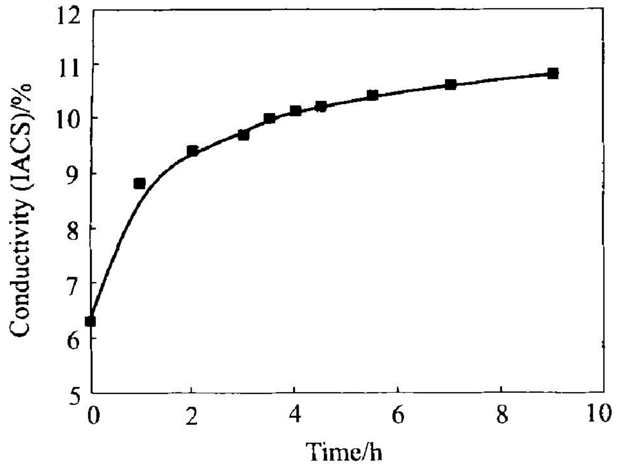

Fig. 5 Relationship between aging time at 380 ℃ and conductivity at room temperature

7.88%[9]. It is known that the conductivity of Cu-Ni-Sn alloy is increased with deformation and ageing time increasing to some extent[10]. It can be seen that the conductivity of Cu-15Ni-8Sn alloy is increased to some degree because of the addition of Si.

The change of conductivity relates to following factors mainly. For Cu-15Ni-8Sn-0.4Si alloy, at first, it occurs spinodal decomposition and forms a modulated structure with Sn-rich zone and Sn-lean zone. The result is that alloying agent is depleted and the probability of electron scattering is reduced so that the conductivity is increased. In addition, at the beginning of ageing dislocation produced by cold roll moves or restructures so that the conductivity of alloy increases very quickly. Subsequently, because γ' ($(Cu, Ni)_3Sn$, coherent with matrix) and γ ($(Cu, Ni)_3Sn$, incoherent with matrix) phases precipitate in turn the conductivity of alloy increases slowly. Considering the change of conductivity is great during recovery and gentle during recrystallization, it can be assumed that early the alloy is in recovery stage. Ageing for 10 h or so, the alloy enters recrystallization stage. During ageing, because of the precipitation of Ni_2Si phase, alloying agent in matrix is depleted further so that the conductivity of experimental alloy is higher than that of Cu-15Ni-8Sn alloy.

Fig. 6 shows the hardening curve of Cu-15Ni-8Sn-0.4Si alloy after ageing at 380 ℃. It can be seen that the hardness curve is single-peaked. At the beginning of ageing, the hardness is increased quickly. After 1h, the hardness is increased to 430 HV from 304 HV in the cold-rolled specimen. It is explained that the alloy has been spinodal decomposition. It reaches the peak of 460 HV or so at 4h. Subsequently, the hardness is decreased to some extent. It is explained that the alloy has entered over ageing stage. However, the hardness is still above 430HV while the maximum of hardness in ordinary Cu-15Ni-8Sn alloys is 430 HV or so.

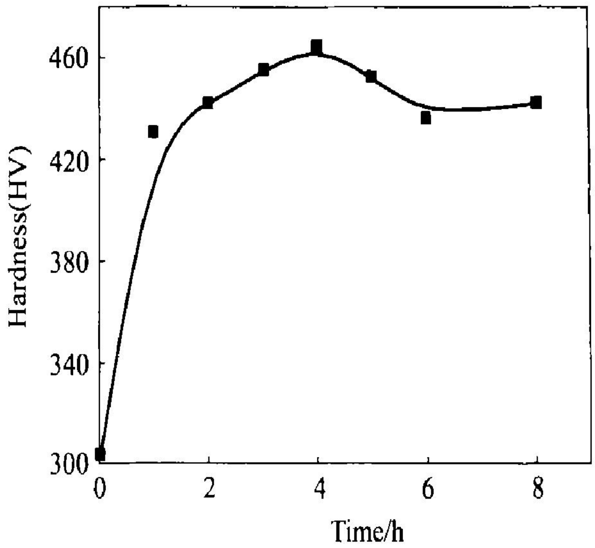

Fig. 6 Relationship between aging time at 380 ℃ and hardness

Cu-15Ni-8Sn alloys generate three phase transitions during ageing. Among them, spinodal decomposition forms fine modulated structure and creates coherent stress field periodically which hinders the movement of dislocation and strengthens alloys. The γ' metastable phase is converted from modulated structure. It is coherent with matrix. Therefore, strengthening effect is strong and the contribution of γ' phase to the strengthening effect is large as well. The γ phase softens the alloy usually. Because γ' phase is converted from modulated structure, it appears following modulated structure. The interval of two strengthening peaks influences the shape of hardening curve. The interval in this alloy is small. Therefore, the hardening curve is single-peaked. During ageing, because the deposit of Ni_2Si phase can produce additional strengthening the hardness of experimental alloy is higher than those of Cu-15Ni-8Sn alloys.

4 DISCUSSIONS

Cu-15Ni-8Sn alloy is strengthened by spinodal decomposition. Strengthening effect is mainly from spinodal decomposition[11, 12]. Fig. 7 shows the TEM images of spinodal decomposition during ageing in Cu-15Ni-8Sn alloy added 0.4% Si. It can be seen that there also exists spinodal decomposition in Cu-15Ni-8Sn-0.4Si alloy, which is still the main source of strengthening. The modulated structure is coarsened after a long time ageing. The coherent stress field produced by the field of component fluctuation periodically is reduced accordingly so that the strengthening effect is reduced. In additional of spinodal decomposition, the alloy is also strengthened by γ' metastable phase. But the interval of them is small.

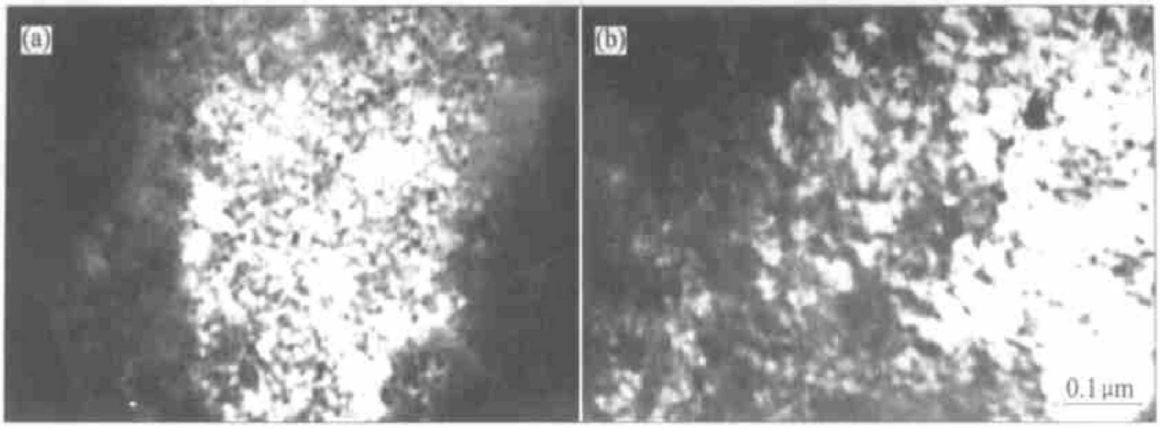

Fig. 7 TEM images of spinodal decomposition of experimental alloy during ageing
(a) —After ageing for 0.5 h; (b) —After ageing for 24 h

Therefore, when the strengthening effect of spinodal decomposition is reduced the hardness is decreased and the alloy enters over ageing stage.

In this paper, the added-Si combines with Ni dominantly and precipitates as new phases of Ni_2Si and Ni_3Si. This has been analyzed in case structure. Ni_3Si phase is difficult to dissolve in matrix and Ni_2Si phase is in reserve. So, after solution only Ni_2Si phase dissolves into matrix and forms supersaturated solid solution. After cold roll, supersaturated solid solution decomposes during ageing. Ni_2Si phase distributes throughout matrix with the formation of small and disperse precipitated phase, which retards the movement of dislocation and results in precipitation strength. The cold roll before ageing also increases the alloy's strength. Ageing procedure is accelerated by the cold roll. Precipitation phase particles are more disperse because of the cold roll. It is indicated that the Ni_2Si new phase makes the Cu-15Ni-8Sn-0.4Si alloy's strength 30 HV higher than ordinary Cu-15Ni-8Sn alloy's.

5 CONCLUSIONS

1) The added-Si combines with Ni dominantly and precipitation as new phases of Ni_2Si and Ni_3Si, which suppresses the discontinuous precipitation of Cu-15Ni-8Sn alloy.

2) During ageing, because of the precipitation of the Ni_2Si phase, the alloying agent is depleted further. So that the conductivity of experimental alloy is increased to some degree.

3) Compared with Cu-15Ni-8Sn alloy, the micro-hardness of experimental alloy is increased because the precipitation of Ni_2Si phase operates additional hardness during ageing.

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