Effect of Ni/Si mass ratio on microstructure and properties of Cu–Ni–Si alloy

Shiping Tao, Zhenlin Lu, Lei Jia, Hui Xie and Jinlong Zhang

1 School of Materials Science and Engineering, Xi’an University of Technology, Xi’an 710084, People’s Republic of China
2 School of Materials Engineering, Xi’an Aeronautical University, Xi’an 710077, People’s Republic of China
3 Author to whom any correspondence should be addressed.
E-mail: lvzl2002@xaut.edu.cn

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Abstract

Cu–Ni–Si alloys with 94 wt% Cu content and different Ni/Si mass ratios were prepared by hot pressing sintering, and then solution treatment and ageing treatment were also performed. Microstructure and phase composition along with electrical conductivity and hardness of the alloys under different treating condition was studied, and then the influence of Ni/Si mass ratio was discussed. Results showed that the as-sintered Cu–Ni–Si alloys mainly consisted of α-Cu matrix and some Ni3Si12 particles at the grain boundary as well as δ-Ni2Si phases inside the matrix. After solution treatment, most of the Ni–Si compounds decomposed, but δ-Ni2Si precipitates from the matrix after ageing treatment. With increasing Ni/Si mass ratio, the electrical conductivity and hardness of the alloys increases firstly and then decreases, while a highest combination of them achieved when the mass ratio of Ni/Si was 4:1. The effect of Ni/Si ratio on the electrical conductivity of Cu–Ni–Si alloys can be mainly ascribed to the residual content of Ni/Si in the Cu matrix after ageing treatment. When the mass ratio of Ni/Si is equal to the atomic ratio of δ-Ni2Si phase, most of the Ni and Si atoms would precipitates as δ-Ni2Si, and then the electrical conductivity reaches the highest value.

1. Introduction

In recent decades, Cu–Ni–Si alloys have attracted extensive research attention due to their good physical and mechanical properties, and have been used broadly in many applications, such as lead frame of large-scale integrated circuits, high-speed rail transit, and optoelectronic devices, and etc [1–4]. With the recent development of lead frame materials for integrated circuits towards high precision and integration, increasing requirements are put forward for the enhanced conductivity and improved mechanical properties of lead frame materials [5]. Cu–Ni–Si alloy is considered as one of the most potential candidates not only due to its high strength, but also high electrical conductivity and excellent cold processing ability [6–8]. Though the strength of the Cu–Ni–Si alloy can be improved by adding alloying elements or optimizing the technological process, the electrical conductivity always declines remarkably [9–11]. Besides this, the traditional production process of Cu–Ni–Si alloy is very complex and costly, where semi-continuous casting ingot, homogenous annealing treatment, hot rolling, solid solution treatment, cold rolling and ageing treatment are applied in turn [12, 13]. In this process, reticular grain boundary always formed during the solidification process due to the out-diffusion of solution atoms from primary phase to residual liquid, especially in Cu–Ni–Si alloys with high Ni and Si addition [14]. Such a reticular grain boundary cannot be eliminated by heat treatments and significantly reduces the mechanical properties and electrical conductivity. In order to break this reticular structure, a number of steps thermal and cold mechanical treatments such as rolling and cold rolling, are essentially required to achieve, leading to the increase on cost and manufacturing period [15].

In the case of powder metallurgy method, the diffusion of atoms is much more difficult than melting and casting method, and thus the formation of reticular structure is expected to suppressed. Moreover, the Ni/Si atoms has been considered to have big influence on the microstructure and properties of Cu–Ni–Si alloys since...
there are two kinds of Ni–Si compounds viz. Ni$_2$Si and Ni$_3$Si[J]. Therefore, Cu–Ni–Si alloy with a total content of 6 wt% but different Ni and Si mass ratios were try to prepared by a powder metallurgy method, and then solution and ageing treating was also performed. Then the microstructure and properties were studied, and then the influence of Ni/Si mass ratio was clarified.

2. Experimental details

In the present study, pure copper, nickel and silicon powder were used as raw materials, and the purity of all the elemental powder is above 99.9 wt%. The particle size of them was 20, 1, and 1 μm, respectively. The nominal compositions of Cu–Ni–Si alloys in the present paper are: Cu content 94 wt%, and Ni/Si mass ratios 2:1, 3:1, 4:1 and 5:1.

The preparation of Cu–Ni–Si alloy was divided into four steps. Firstly, the raw powders and zirconia ball were weighed and added into a ball grinding tank, where the ratio of mass of zirconia ball to the material mass was 2:1. Secondly, the elemental powders were mixed by a planetary ball mill at 200 r min$^{-1}$ for 12 h, and Ar gas was used as protection atmosphere. Thirdly, the powder mixture was sintered by using a hot-pressed sintering furnace (ZT-40-20Y) at 960 for 1 h, where the heating rate was 10 °C min$^{-1}$, hot pressing pressure was 30 MPa and vacuum of the furnace chamber was lower than 0.1 Pa. Fourthly, the sintered Cu–Ni–Si alloy blocks were treated by solid solution at 900 °C for 2 h and ageing at 450 °C for 4 h.

Microstructure and chemical composition were analyzed by a scanning electron microscopy (SEM, JSM-6510A) equipped with energy diffraction spectrum (EDS, Oxford) phase composition was investigated by a x-ray diffractometer (XRD, PANalytical), respectively. Hardness and electrical conductivity were measured by an electric durometer (HBRV-187.5) and an eddy current conductivity meter (Sigma-2008B1).

3. Results and discussion

3.1. Microstructure of Cu–Ni–Si alloys

Figure 1 shows XRD patterns of Cu–Ni–Si alloys under different treating conditions. It can be found that, showing the existence of α–Cu phase and Ni$_{13}$Si$_{12}$ and δ-Ni$_2$Si phases in all the sintered alloys, and the amount of Ni–Si compounds is very limited because of the weak diffraction peaks. After solution and solution + ageing treatment, there is almost only α–Cu phase deduced from the XRD patterns, but high magnification patterns show that there is δ-Ni$_2$Si phase in the solution + ageing Cu–Ni–Si alloys when the Ni/Si mass ratio is lower than 5:1.

Figure 2 shows the microstructure of Cu–Ni–Si alloys prepared by hot pressing sintering. It can be found that, there are particle-like phase among the grain boundary of Cu matrix, and some small particle- or needle-like phase inside the Cu matrix grains. Combining the results of EDS (Table I) analysis and XRD patterns, it can be confirmed that the particle-like phase at the grain boundary is Ni$_{13}$Si$_{12}$, while the particle- or needle-like phase inside the grains is Ni$_2$Si. The formation of such a microstructure can be described as follows. Firstly, Cu and Ni powder start to soften and deform with the assist of pressure and increased sintering temperature, and thus there is increasing dense contact between different elemental powders. Moreover, the diffusion rate of atoms increases gradually due to the adhesion of the surface of the copper, nickel, and silicon particles as well as the high temperature. Secondly, Ni and Si can react with each other to form the Ni$_3$Si$_2$ phase at grain boundary, along with the dissolving of Ni and Si atoms into Cu matrix, and the formation of Cu(Ni$_2$Si) solution. Finally, when the sintering process is finished, the temperature cools down slowly since the excellent heat-retaining ability of the vacuum furnace. As a result, Ni$_2$Si particles or needle-like phase would precipitate from the supersaturated Cu(Ni$_2$Si) solution, which has been already demonstrated by many published literature [16, 17].

Figure 3 shows the microstructure of as-sintered Cu–Ni–Si alloys after solid solution treatment at 900 °C for 2 h. It can be found that, compared with the as-sintering state, all the Ni$_{13}$Si$_{12}$ and δ-Ni$_2$Si precipitates disappear after solution treatments, leaving the clean grain boundaries and Cu grains. Such a result of microstructure observation also agrees with that of XRD analysis. According to the previous work on the Cu–Ni–Si alloys by melting and casting method, it is the same that Ni$_2$Si can be decomposed and re-solute into Cu matrix by solution treatment, but a new find is the Ni–Si compounds at the grain boundary can also be eliminated at the same time, which is value to studying in our future work. Microstructure of Cu–Ni–Si alloys after ageing treatment is shown in figure 4. It can be found that, when the Si content is high, viz. the mass ratio of nickel-silicon is 2:1 and 3:1, a large number of excess Si atoms get distributed at the grain boundary in the form of elemental substance and a small amount of δ-Ni$_2$Si particles precipitate at the grain boundary since the rapid diffusion rate (figures 4(a) and (b)). However, there is no particle- or needle-like precipitates inside the Cu matrix as that of as-sintered sample, which doesn’t agree with the XRD patterns and may be ascribed to the small size of the precipitations [18]. When the Ni/Si mass ratio increases to 4:1, the amount of both elemental Si...
Figure 1. XRD patterns of alloys Cu–Ni–Si alloys under different processing conditions, where the Ni/Si mass ratios are (a) 2:1, (b) 3:1, (c) 4:1 and (d) 5:1, respectively.

Figure 2. SEM images of as-sintered Cu–Ni–Si alloys with mass Ni/Si ratios of (a) 2:1, (b) 3:1, (c) 4:1 and (d) 5:1, respectively.
particles and small Ni$_2$Si particles at the grain boundary decreases significantly, while there is a large amount of flocculent grains as shown in figure 4(c). High magnification observation indicates there are fiber-like phase inside the Cu matrix, as shown in figure 4(c1). When the Ni/Si ratio 5:1, there is very limited flocculent grains (figure 4), and thus it can be speculated these fibrous phase is δ-Ni$_2$Si according to the change of the XRD patterns.

Such a difference among the Cu–Ni–Si alloys with different Ni/Si ratio can be explained approximately by the Cu-Si binary phase diagram, since the absent of Cu–Ni–Si ternary phase diagram. When the Ni/Si mass ratio is low, the Si content is high, and then Si would exist as elemental powder since the solution ability of Si in Cu is limited [19]. It is of course to mention that, though the solution ability of Si in Cu is much higher than the content of Si in this paper, according to the Cu-Si binary phase diagram, the solution ability of Si may be changed when there is a Cu–Ni–Si ternary system. With the increase of Ni/Si mass ratio, the real Si content decreases but Ni content increases in the Cu–Ni–Si alloys, and hence it is easy to understand that the amount of elemental Si particles would decreases. On the other hand, the content of Ni and Si in Cu is suitable for the formation of Ni$_2$Si when the Ni/Si mass ratio is 4:1, which corresponds to the mole ratio of about 2:1, leading to the formation of a large number of fiber like Ni$_2$Si precipitation.

### 3.2. Electrical and mechanical properties of Cu–Ni–Si alloy

Figure 5 shows the electrical conductivity and Vickers hardness of Cu–Ni–Si alloy under different treating conditions. Apparently, the electrical conductivity of the as-sintered alloys increases gradually with increase of Ni/Si mass ratio, which reaches the maximum value of 33.2 %IACS when the mass ratio of Ni to Si is 4:1. However, the hardness does not change notably and the maximum is 143.12 HV at the Ni/Si ratio of 3:1.

| Region | Cu (at%) | Ni (at%) | Si (at%) |
|--------|----------|----------|----------|
| A      | 11.04    | 63.20    | 25.76    |
| B      | 21.04    | 51.43    | 27.55    |

Table 1. EDS results of hot pressing sintering alloys (at%).
suggesting that the electrical conductivity is more sensitive to the Ni/Si mass ratio than hardness. Such a phenomenon is because that the significant difference of the damage of Ni and Si solution atoms on the electrical conductivity of Cu matrix [20]. After solid solution treatment, the conductivity the Cu–Ni–Si alloys decreases obviously since the decompose of Ni$_2$Si phase and the solution of its products Ni and Si atoms, while the small decrease of hardness is due to the increase of grain size of Cu matrix. A big increase of both electrical conductivity

Figure 4. SEM micrographs after solution + ageing treatment of Cu–Ni–Si alloys with Ni/Si mass ratios are (a) 2:1, (b) 3:1, (c) 4:1 and (d) 5:1, respectively.
and hardness can be found after the subsequent ageing treatment, which can be attributed to precipitation of Ni$_2$Si from the Ni and Si solute atoms.

It is known that Cu–Ni–Si alloy is a typical solid solution ageing strengthening material [21–26], and hence the influence of Ni/Si mass ratio on the properties of Cu–Ni–Si alloys should be discussed based on the results of the alloys after solution + ageing treatment. According to the application domains of Cu–Ni–Si alloys, the combination of high strength and electrical conductivity is always required, and thus the best combination properties should be achieved at the Ni/Si mass ratio of 4:1, where the electrical conductivity and hardness are 34.47 %IACS and 261.7 HV, respectively. The combination properties, especially the electrical conductivity reaches the highest at the mass ratio of 4:1, can be explained from the viewpoint of phase composition. As we definite before, the main phase composition of Cu–Ni–Si alloys is Cu and Ni$_2$Si precipitates. Then, the minimum residual solution of Ni or Si atoms should achieved when the atomic ratio between them is about 2:1, viz. the mass ratio of 4:1. Moreover, when the residual solution atom is the minimum, namely, most of the Ni and Si atoms form Ni$_2$Si during the ageing process, the electrical conductivity gets the highest values, since the damage of precipitated is much lower than that of solution atoms.

4. Conclusions

1. The Cu–Ni–Si alloy prepared by hot pressing sintering mainly consists of the primary $\alpha$-Cu matrix, some Ni$_3$Si$_{12}$ particles at the grain boundary and particle- or needle-like $\delta$-Ni$_2$Si precipitation inside the Cu matrix. All the Ni–Si compounds disappear after solution treatments, but $\delta$-Ni$_2$Si phase precipitates again during the ageing treatment.

2. Electrical conductivity and Vickers hardness of Cu–Ni–Si alloy increases first and then decreases with the increase of Ni/Si mass ratio, but the and the combination properties reaches the highest values when the mass ratio is 4:1.

3. The influence of Ni/Si mass ratio on the electrical conductivity of Cu–Ni–Si alloys can be mainly attributed to the residual Ni or Si atoms in Cu matrix. When the mass ratio is 4:1, namely the atomic ratio is about 2:1, most of the Ni and Si atoms can precipitates as $\delta$-Ni$_2$Si phase, resulting the highest value of electrical conductivity.

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ORCID iDs

Shiping Tao  https://orcid.org/0000-0003-4255-9040
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