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Effect of high contents of nickel and silicon on the microstructure and properties of Cu–Ni–Si alloys

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**Abstract**

Cu–Ni–Si alloys have been widely used in electronics and electrical industries. The preparation method of alloy was not limited to smelting, powder metallurgy method has also attracted the attention of many researchers. In this study, Cu–Ni–Si alloys were prepared using hot-pressed sintering and elemental copper powders, in which nickel and silicon powders were used as raw materials. The results show that, when the Cu–Ni–Si alloys were prepared using hot-pressed sintering, there were no Ni-Si intermetallic compounds except the \(\delta\)-Ni\(_2\)Si phase in the microstructure of alloys. After the ageing treatment, when the mass ratios of Ni/Si were 2:1 and 3:1, the precipitation of \(\delta\)-Ni\(_2\)Si phase was significantly less. However, when the mass ratios of Ni/Si were 4:1 and 5:1, the precipitation of \(\delta\)-Ni\(_2\)Si phase particles increased significantly. The results from electrical conductivity and Vickers hardness show that, after the ageing treatment, both the electrical conductivity and Vickers hardness of the alloys greatly improved.

1. Introduction

Cu–Ni–Si alloy has attracted extensive attention in recent years due to its good physical and mechanical properties, especially in the lead frame of large-scale integrated circuits, high-speed rail transit, optoelectronic devices, microwave technology, aerospace, defense industry, electronics industry and home appliance industry connectors [1–6]. Moreover, Cu–Ni–Si alloy has been one of the few advanced materials critical for the development of nations. The integrated circuit has become the core of modern electronic engineering, and its most critical component is the lead-frame, which requires the use of materials with high electrical conductivity and strength [7, 8]. However, a perfect lead-frame material generally requires the Vickers hardness, conductivity and tensile strength of more than 180 HV, 80% IACS and 600 MPa, respectively [9]. It is well known that, for copper, higher the strength, lower the conductivity is, and vice versa. According to the theory of metal electronics, it is necessary to reduce the impurity scattering to achieve higher conductivity. However, in order to increase the strength of the copper alloy, it must use various reinforcement methods, such as adding alloying elements, and improve the machining process. Nevertheless, all these improved methods can produce impurity scattering, which will reduce the conductivity of copper alloy [10–13]. On the other hand, in terms of alloy preparation technology, at present, the traditional process of producing Cu–Ni–Si alloy is the semi-continuous casting ingot - homogeneous annealing - hot rolling-solid solution treatment-cold rolling-aging treatment [14, 15]. However, this process of preparing Cu–Ni–Si alloy has a slow cooling rate, and the solidification process can easily form a network of reticulated grain boundary phase. Moreover, after the solution and aging treatments, the reticular grain boundary is not only difficult to disappear, but also the size range of the precipitates is relatively wide, leading to a decline in the comprehensive performance of the alloy [16, 17]. When heat treatment and machining is used, the alloy is easy to crack during rolling and forging. However, the powder metallurgy method can effectively avoid the occurrence larger of Ni and Si compounds, and in recent years, it has been reported that Cu–Ni–Si alloy materials were prepared by powder metallurgy [18–22]. Compared with
literature [21, 22], this paper not only cancelled the Ar protection measures in the ball milling process, but also reduced the ball milling speed and shortened the ball milling time. On the other hand, when the Cu content was reduced and Ni and Si were increased, the electrical conductivity of Cu–Ni–Si alloy does not decrease, but the mechanical properties of the alloy were improved by 12.1%. It provides a theoretical basis for Cu–Ni–Si alloys with high nickel and silicon contents in the research and practical application of high strength and high conductivity materials.

Thus, this study aims to understand the preparation of Cu–Ni–Si alloy with high content of Ni and Si using elemental Cu, Ni and Si powders as raw materials, and explore the effect of solution treatment and aging on the microstructure and properties of Cu–Ni–Si alloy to provide theoretical basis for obtaining high performance.

2. Experimental

Cu (with the purity and D50 of 99.9% and 20 μm), Ni (with the purity and D50 of 99.9% and 1 μm) and Si (with the purity and D50 of 99.9% and D50 1 μm) powders were used as the raw materials, which were bought from Sinopharm Chemical Reagent Co. Ltd, China, as shown in figure 1. It can be seen that, Cu, Ni and Si powders possessed the typical morphologies that they show when prepared using electrolyzation, and mechanical disruption methods. The D50 sizes of the powders agreed well with their nominal sizes. For each set of experiment, the content of Cu was fixed to be 90 wt%, whereas the mass ratio of Ni/Si was varied through values of 2:1, 3:1, 4:1 and 5:1. The chemical composition of Cu–Ni–Si alloy was shown in table 1.

According to the desired composition, choose 5 mm and 10 mm diameter zirconia balls and alloy powders were weighed, and the two sizes of zirconia balls accounted for 50 percent each, and ground in the ball mill. The mass of zirconia balls and alloy powder mass ratio was 2:1. Furthermore, the rotation speed was set at 200 r min \(^{-1}\) and uniform ball-grinding was conducted for 12 h. The hot-pressed sintering process was carried
out on the ZT-40-20Y hot-pressed sintering furnace equipment. More specifically, after the ball grinding, the alloy powders were placed in the graphite grinding tool and a pre-pressure of 5 MPa was applied on them before sintering. After holding the pressure for 5 min, the pressure was increased to 30 MPa. At the same time, the temperature was increased to 960 °C with the heating rate of 10 °C min⁻¹. After holding the temperature at 960 °C for 1 h, the mixture was cooled down to room temperature in the furnace. The sintered alloys were treated using solid solution at 900 °C for 2 h and aged at 450 °C for 4 h.

The original sample of hot-pressed sintering was φ40 mm × 15 mm, and then cut into φ12 mm × 12 mm by wire-electrode cutting for analysis and testing. The microstructure was mainly analyzed using a Japanese electronic JSM-6510A scanning electron microscope (SEM). X-ray diffraction (XRD) analysis using PANalytical x-ray diffractometer, and the test Angle was 30 to 80 degrees and the test process was 10 degrees per minute. The transmission electron microscopy using an FEI Talos F200x microscope. Moreover, Relative density was measured by the Archimede’s method. The Vickers hardness was measured using an HBRV-187.5 electric Brinell Hardness tester, and Five test points on the sample surface were selected to calculate the average value, in which the pressure load was 2 kg and the pressure was maintained for 30 s. The conductivity was measured by Sigma2008B1 type eddy current conductance instrument for five times and then the average value was calculated.

3. Results and discussion

3.1. Phase and microstructure of Cu–Ni–Si alloy

The XRD patterns of Cu–Ni–Si alloys with different heat treatments are presented in figure 1. It can be seen that there were α-Cu and δ-Ni₃Si phases and Si atoms in the alloys. Higher the content of Ni, stronger was the diffraction peak of δ-Ni₃Si phase in the hot-pressed sintered Cu–Ni–Si alloys. After solution treatment, the diffraction peak of δ-Ni₃Si phase in the alloys became weaker, especially when the mass ratio of Ni/Si was 2:1, which is when the δ-Ni2Si phase completely disappeared (figure 2(b)). It indicates that, after the solution treatment, a part of δ-Ni₃Si phase was dissolved into the Cu matrix. After ageing treatment, the diffraction peak of δ-Ni2Si phase decreases, and indicating that the size and quantity of precipitated phase change obviously. (figure 2(c)).
Figure 3 shows the SEM image of Cu–Ni–Si alloys prepared using hot-pressed sintered method. It can be seen that the alloy mainly consisted of strip and granular primary phase, and a small amount of black particles existed at the grain boundary (Figure 3(b)). When the mass ratio of Ni/Si was 5:1, the black particle phase disappeared (Figure 3(d)).

As shown in Figure 4, the transmission analysis shows that the Ni$_3$Si phase was on the grain boundary and the black particles were the Si atoms. Combined with the XRD analysis shown in Figure 2, it can be seen that, when the content of Si was high in hot-pressed sintering, there were residual Si atoms in the alloy. When the Ni content was gradually increased, the strip δ-Ni$_2$Si phase at the grain boundary gradually increased, while the granular δ-Ni$_2$Si phase in grains gradually decreased.

This is because, with the increase of sintering temperature, the Cu–Ni–Si alloy powders began to soften and deform under the action of pressure. Meanwhile, the diffusion of atoms increased gradually, and the adhesion on the surface of the copper, 3:1. Bright-filled image along with selective area electron diffraction (SAED) patterns. nickel and silicon particles began the alloying process. In the process of sintering alloying, the driving force mainly comes from the free energy of the atom itself. Therefore, nickel and silicon can initiate the alloying reaction to generate primary phase at the grain boundary, which evident from the white particles phase that
slowly stabilized and saturated. However, the rest of Ni and Si atoms will continue to react in the copper matrix through atomic diffusion, and form tiny precipitates in the grain boundary. The quantity and distribution of precipitates is mainly related to the contents of Ni and Si. When the mass ratios of Ni to Si were 2:1, 3:1 and 4:1, because of the low content of Ni, it could completely react with Si, and the remaining Si atoms agglomerated at the grain boundary (figure 3). When the mass ratio of Ni to Si was 5:1, only $\delta$-Ni$_2$Si was generated in the alloy.

According to a previous study $^{[23]}$, the difficulty of forming intermetallic compounds is mainly related to the formation enthalpy. However, the enthalpy of mixing of Ni–Si ($\sim 40$ kJ mol$^{-1}$) was higher than that of Cu–Si ($\sim 19$ kJ mol$^{-1}$) and Cu–Ni (4 kJ mol$^{-1}$) in the Cu–Ni–Si alloy. Therefore, in the process of hot-pressed sintering, Ni and Si preferentially formed a structure, which eventually evolved into Ni-Si phase.

On the other hand, the formation enthalpy can be used to measure the ability of intermetallic compounds to form $^{[24]}$, and the enthalpy of the formation of Ni$_x$Si$_y$ phase can be calculated using equation (3-1).

$$\Delta H(Ni_xSi_y) = \frac{E^{NiSi}_{tot} - xE^{Ni}_{atom} - yE^{Si}_{atom}}{x + y} \quad (3-1)$$

where $E^{NiSi}_{tot}$ is the total energy of an intermetallic compound at equilibrium lattice parameters, $E^{Ni}_{atom}$ and $E^{Si}_{atom}$ are the atomic energies of Ni and Si at equilibrium lattice parameters, respectively, $x$ is the number of Ni atoms in the unit cell, and $y$ is the number of Si atoms in the unit cell. The formation enthalpy of Ni$_{13}$Si$_{12}$, Ni$_3$Si and $\delta$-Ni$_2$Si phases were $-0.5218$ eV Atom$^{-1}$, $-0.4607$ eV Atom$^{-1}$ and $-0.6175$ eV Atom$^{-1}$ respectively, which calculated according to equation (3-1). And further proving that $\delta$-Ni$_2$Si phase was more capable of forming than other phases.

The ability to form intermetallic compounds can also be measured by binding energy $^{[25]}$. The binding strength mainly depends on the absolute value of binding energy. Higher the absolute value of binding energy, higher is the binding strength, and vice versa. The binding energy can be calculated using equation (3-2).

$$\Delta E(Ni_xSi_y) = \frac{E^{NiSi}_{tot} - xE^{Ni}_{atom} - yE^{Si}_{atom}}{x + y} \quad (3-2)$$

where $E^{NiSi}_{tot}$ is the total energy of the alloy phase at the equilibrium lattice constant, $E^{Ni}_{atom}$ and $E^{Si}_{atom}$ are the atomic energies of Ni and Si elements at equilibrium lattice parameters, $x$ is the number of Ni atoms in the unit cell, and $y$ is the number of Si atoms in the unit cell. The binding energies of Ni$_{13}$Si$_{12}$, Ni$_3$Si and $\delta$-Ni$_2$Si phases were $-4.1203$ eV Atom, $-4.8774$ eV Atom and $-5.0548$ eV Atom, which calculated according to equation (3-2). It shows that The binding energy of the $\delta$-Ni$_2$Si phase was higher than other phases.

Figure 5 shows the microstructure of alloys after 2 h of solution treatment at 900 °C. It can be seen that, when the mass ratio of Ni to Si was 2:1, the $\delta$-Ni$_2$Si phase in the alloy was solid and dissolved into the Cu matrix. Only
the rich Si residue was observed in the system. When the mass ratio of Ni to Si was 3:1, the granular $\delta$-Ni$_2$Si phase was mostly dissolved into the Cu matrix, while the bulk $\delta$-Ni$_2$Si phase and Si did not show significant change (figures 5(b), and (B)). Additionally, when the Ni to Si mass ratios were 4:1 and 5:1, the granular $\delta$-Ni$_2$Si phase was all dissolved into the Cu matrix, while the bulk $\delta$-Ni$_2$Si phase did not show any change (figures 5(c), and (d)).

After the ageing treatment, the microstructures of Cu–Ni–Si alloys are shown in figure 6. As seen from figures 6(a)–(d), except for the $\delta$-Ni$_2$Si phase at the grain boundary, a smaller second phase was also precipitated in the trans-granular phase. The XRD analysis presented in figure 2(c) shows that the second precipitated phase was the $\delta$-Ni$_2$Si phase. The size of precipitated phase was smaller than that of the hot-pressed sintering method. Moreover, when the Ni to Si mass ratios were 4:1 and 5:1, the amount of precipitated phase was higher. It is well known that the Cu–Ni–Si alloy is a typical solid solution aging reinforced alloy material [26, 27], and there are as many as seven kinds of Ni–Si structures [28–33]. These include two Ni$_3$Si phases ($\beta$-Ni$_3$Si and $\iota$-Ni$_3$Si), one $\gamma$-Ni$_5$Si$_2$ phase ($Ni_{31}Si_{12}$), two Ni$_2$Si phases ($\delta$-Ni$_2$Si and $\theta$-Ni$_2$Si), one $\varepsilon$-Ni$_5$Si$_2$ phase and one $\omega$-NiSi phase. According to the first principles, the $\delta$-Ni$_2$Si phase is the most stable phase with low enthalpy of formation [34]. Therefore, $\delta$-Ni$_2$Si phase was finally formed in the Cu–Ni–Si alloy after heat treatment, which was consistent with the results published in some previous works [35, 36].

3.2. Properties of Cu–Ni–Si alloy
Physical density and relative density of the Cu–Ni–Si alloys in different states were calculated and shown in table 2. The physical density of Cu–Ni–Si alloys increase with the decrease of Si, because the addition of Si is relatively light (theoretical density 2.33g cm$^{-3}$). And the relative density of Cu–Ni–Si alloy after ageing treatment was higher than that of other heat treatment.

![Figure 6. SEM images of ageing treatment which have magnified 300 and 5000 and with the Ni/Si mass ratios of (a) 2:1, (b) 3:1, (c) 4:1, and (d) 5:1.](image-url)
The conductivity and Vickers hardness of Cu–Ni–Si alloys are shown in figure 7. As seen from figure 7 (a), after hot-pressed sintering, the electrical conductivities of alloys increased with the increase of Ni content. After the solid solution treatment, the electrical conductivities of alloys significantly decreased. However, after the ageing treatment, the electrical conductivities of alloys increased with the increase of Ni content. When the mass ratio of Ni to Si was 4:1, the electrical conductivity had the maximum value of 39.33%IACS.

According to a previous work [9], the electrical conductivities of Cu–Ni–Si alloys are related to Ni and Si solute atoms in the alloy. When the numbers of Ni and Si atoms in the Cu matrix are less, the electrical conductivity of the alloy is higher. Figure 3 shows that, when the mass ratio of Ni to Si was less than 4:1, there were obviously surplus Si atoms in the alloy microstructure, which resulted in Si-rich regions in the Cu matrix, thus reducing the electrical conductivities of alloys. After solid solution, large numbers of Ni and Si solute atoms were incorporated into the alloys. The scattering effect of solid solution atoms in the matrix on electrons impeded the movement of free electrons. Therefore, higher the number of solid solution atoms in the matrix, stronger was the scattering capability of electrons, and lower was the electrical conductivity of the alloy. However, after the ageing treatment, Ni and Si atoms in the solid solution of the alloy precipitated out in the form of $\delta$-Ni$_2$Si, which purified the matrix of the alloy and greatly improved the electrical conductivity.

The Vickers hardness values of the alloys are shown in figure 7 (b). It can be seen that the Vickers hardness of the alloy first increased, and then, decreased. After the ageing treatment, when the mass ratio of Ni to Si was 3:1, the maximum Vickers hardness of the alloy was 282.07 HV. Furthermore, when the mass ratio of Ni to Si was 4:1, the minimum Vickers hardness of the alloy was 230.95 HV. This is because the $\delta$-Ni$_2$Si phase precipitated after the ageing treatment, and could effectively prevent the dislocation and grain boundary sliding, thus increasing the hardness of the alloy. Based upon these results, it can be inferred that Cu–Ni–Si alloys having Ni to Si mass ratio of 4:1 with 4 h ageing exhibit the best comprehensive performance.

4. Conclusions

1. There were no Ni-Si intermetallic compounds except for the $\delta$-Ni$_2$Si phase in the Cu–Ni–Si alloys, which were prepared using the powder metallurgy method. Moreover, the $\delta$-Ni$_2$Si phase was more evenly distributed and smaller in size.
2. After the ageing treatment, when the mass ratios of Ni to Si were 2:1 and 3:1, a little fibrous $\delta$-Ni$_3$Si phase was precipitated. When the mass ratios of Ni to Si were 4:1 and 5:1, the amount of fibrous $\delta$-Ni$_2$Si phase increased significantly.

3. The electrical conductivity and Vickers hardness of the alloys with four components in different states were tested. After the ageing treatment, when the mass ratio of Ni to Si was 4:1, both the electrical conductivity and Vickers hardness of alloys greatly improved. The electrical conductivity was 39.33% IACS, whereas the Vickers hardness was 230.95 HV.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Declaration of interests

The authors declared that they have no conflicts of interest to this work.

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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