Effect of high content 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 applied in electronic and electrical industries.The effect of precipitation on the microstructure and properties of the alloys are still not well understood. In this study, Cu-Ni-Si alloys were prepared by hot-pressed sintering and elemental copper powders, nickel powders and silicon powders as raw materials. The results show that, there were no Ni-Si intermetallic compounds except the δ-Ni_2Si phase in the microstructure by hot-pressed sintered preparation of Cu-Ni-Si alloys. And the distribution of the δ-Ni_2Si phase in the alloy was more uniform and smaller. After aging treatment, when the mass ratio of Ni and Si were 2:1 and 3:1, the precipitation of δ-Ni_2Si phase was significantly less, and when the mass ratio of Ni and Si were 4:1 and 5:1, the precipitation of δ-Ni_2Si phase particles increased significantly.The test results by electrical conductivity and vickers hardness show that after ageing treatment, both the electrical conductivity and vickers hardness of the alloys were greatly improved. When the electrical conductivity was 39.33%IACS, the vickers hardness was 230.95HV, and the Cu-Ni-Si alloy had the best comprehensive performance.

Key words: Cu-Ni-Si alloy; Ageing treatment; Precipitated phase; Electrical conductivity; Hot-pressed sintering

1. Introduction

Cu-Ni-Si alloy has attracted extensive attention due to its good physical and mechanical properties in recent decades, 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, etc[1-6]. Thus, it has been one of the advanced materials for the development of countries.The integrated circuit has become the core of modern electronic engineering, and the most critical core component is the lead-frame，and there are higher requirements on the conductivity and strength of lead-frame materials[7-8]. However, A perfect lead-frame material generally requires the following properties: the vickers hardness higher than 180HV, the conductivity higher than 80%IACS, and the tensile strength higher than 600MPa[9]. It is well known that the high strength and high conductivity of copper are contradictory. According to the theory of metal electronic knowable, want to get the maximum conductivity, it is necessary to reduce the impurity scattering, but 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, etc, But it is a pity that 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 semi-continuous casting ingot - homogeneous annealing - hot rolling-solid solution treatment-cold rolling-aging treatment[14-15]. However, this process of the preparation of Cu-Ni-Si alloy due to the slow cooling rate, and solidification process easy to form a network of reticulated grain boundary phase, after the solution and aging treatment, the reticular grain boundary is not only difficult to disappear but also the precipitate phase size is relatively large, and eventually lead to a decline in the comprehensive performance of the alloy[16-17]. In order to obtain better microstructure, it is important to optimize the preparation process.In this study, Cu-Ni-Si alloy with smaller primary phase and more uniform distribution was prepared by using powder metallurgy technology,which eliminated the adverse effect in the early stage and optimized the microstructure of the alloy, and further improved the comprehensive properties of the alloy.

2. Experimental procedure

In the present work, elemental copper powders, nickel powders and silicon powders as raw materials, and the purity of all the elemental powder is above 99.9wt %. The size of the electrolytic copper powders, silicon powders and nickel powders is 20 μm, 1 μm and 1 μm, respectively.The experiment was divided into four groups, in which the content of Cu was 90 wt.%, and the mass ratios of Ni/Si were 2:1, 3:1, 4:1 and 5:1.

According to the composition design, weigh the alloy powders and different sizes of zirconia ball together into the ball grinding tank, and the mass of zirconia ball and the material ratio was 2:1, rotation speed was set at 200 r/min and uniform ball-grinding for 12 hours. The hot-pressed sintering process was carried out on the ZT-40-20Y hot-pressed sintering furnace equipment. The specific operation is to put the alloys powder after ball grinding into the graphite grinding tool and apply a pre-pressure of 5 MPa before sintering. After holding the pressure for 5 min, the pressure starts to increase to 30 MPa. At the same time, the temperature starts to rise to 960 °C with the heating rate of 10 °C/min and then held for 1 h, followed by cooled down to room temperature in the furnace. The sintered alloys samples were treated by solid solution at 900 °C for 2 h and ageing at 450 °C for 4 h.

Microstructure and energy spectrum were analyzed by JSM-6510A scanning electron microscope, XRD spectrum was obtained by PANalytical X-ray diffractometer, and vickers hardness was measured by HBRV-187.5 electric brovie durometer, and the conductivity was measured by Sigma-2008B1 eddy current conductometer.

3. Results and discussion

3.1 Microstructure of Cu-Ni-Si alloy

The XRD patterns of the Cu-Ni-Si alloys in different heat-treated conditions are presented in figure 1. It can be seen that there are α-Cu phase and δ-Ni_2Si phase and Si atoms in the alloys. With the increase of Ni content, the stronger the diffraction peak of δ-Ni_2Si phase in the hot-pressed sintered Cu-Ni-Si alloys. After solution treatment, the δ-Ni_2Si phase diffraction peak in the alloys became weaker, especially

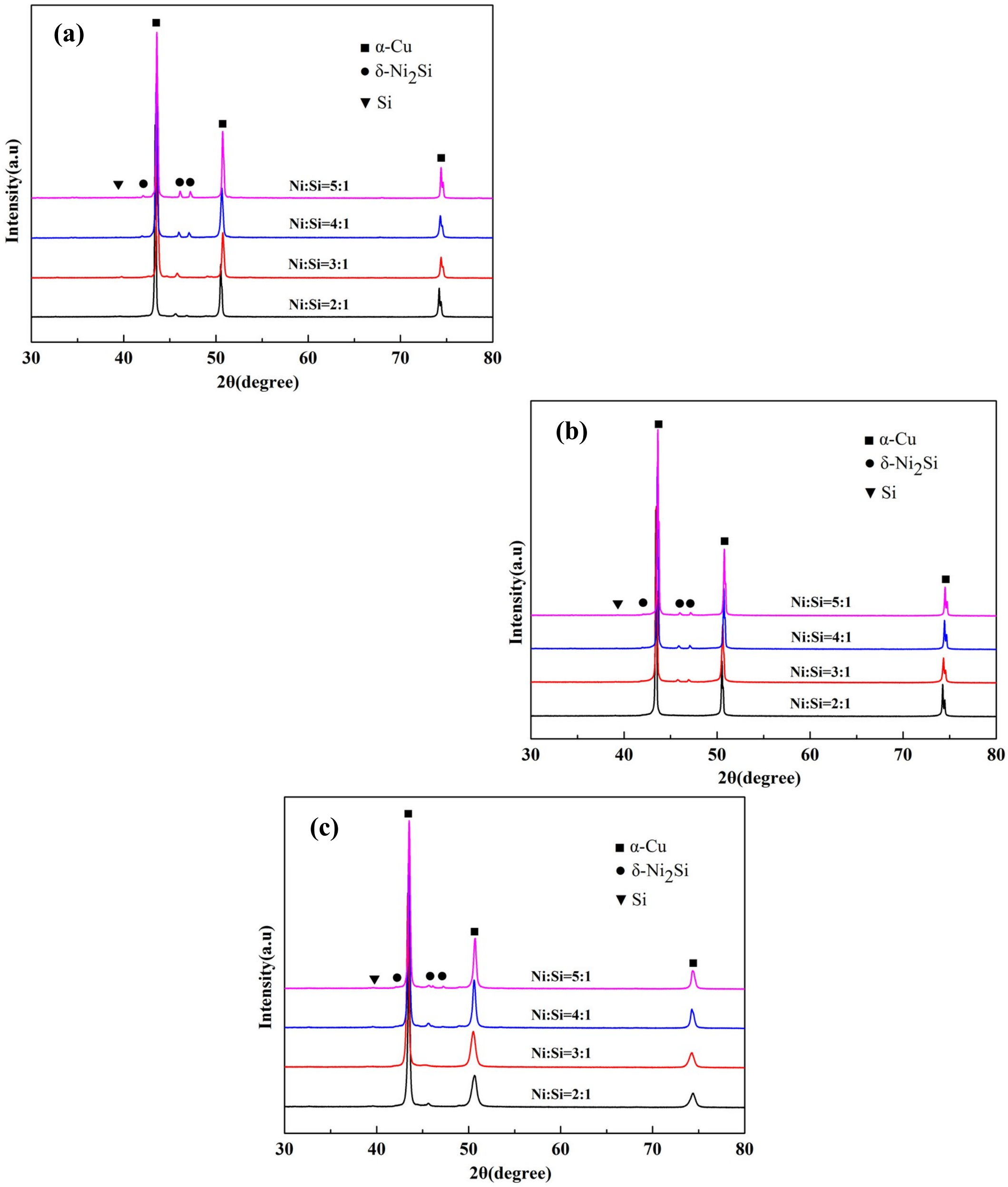


Fig. 1. XRD patterns of samples at different processes

(a) Hot-pressed sintered, (b) Solid solution treatment, (c) Ageing treatment.

when the mass ratio of Ni and Si is 2:1, the δ-Ni2Si phase disappeared directly (Fig. 1a). It indicates that after the solution treatment, a part of the δ-Ni2Si phase has been dissolved into the Cu matrix (Fig. 1b). After ageing treatment there is only δ-Ni_2Si phase was found in the alloys (Fig. 1c).

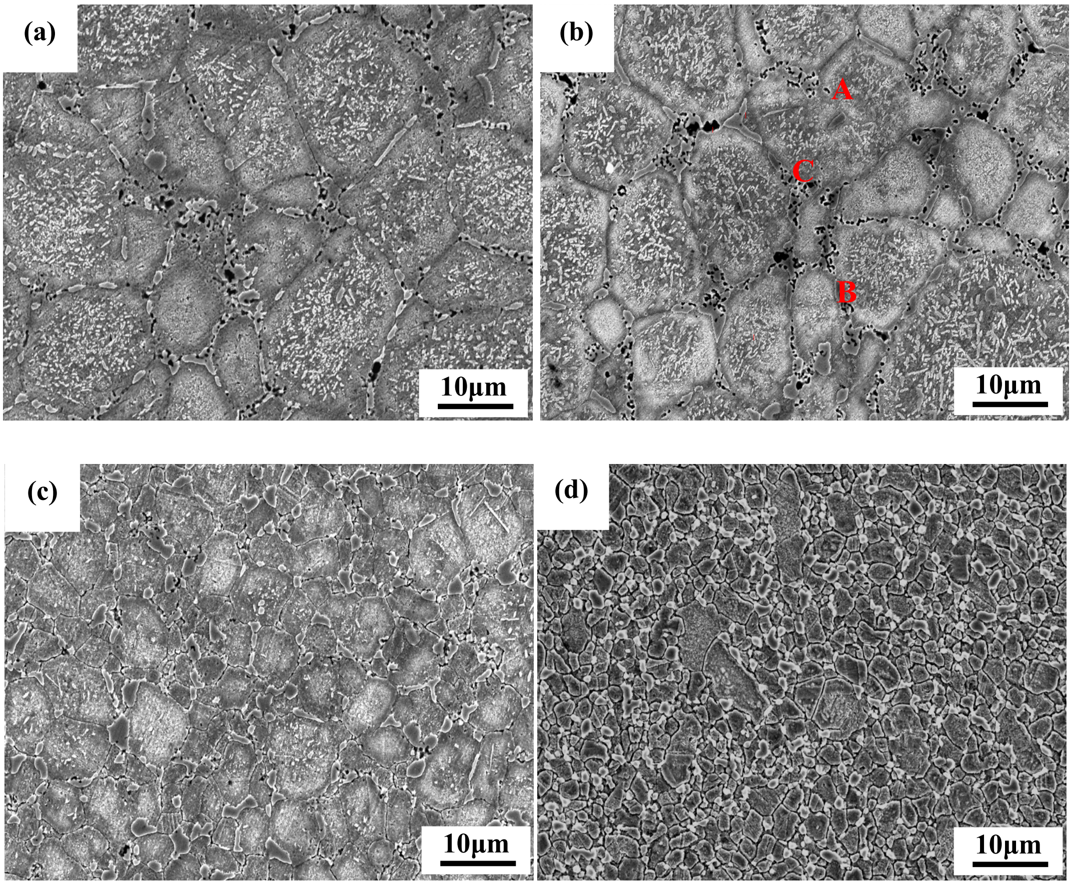


Fig. 2. SEM images of hot-pressed sintered and the mass ratio of Ni and Si (a)2:1, (b)3:1, (c)4:1, (d)5:1.

Fig. 2 shows the SEM image of Cu-Ni-Si alloys prepared by hot-pressed sintered. It can be seen that the alloys mainly consists of two phases: the bulk primary phase at the grain boundary and the granular primary phase inside the grain, and there was also a small amount of black grain phase at the grain boundary (Fig. 2b). According to the EDS chemical composition of the alloys in table 1, The Ni/Si atomic ratios in regions A and B are 1.85:1 and 1.80:1, which are approximately 2:1. According to the XRD analysis in figure 1 (a), it can be determined that the precipitation phase of the block at the grain boundary and the granular primary phase inside the grain are both δ-Ni_2Si phase. While in the C region the content of Si is much higher than other elements, which can be defined as rich Si. It can also be seen from the figure that the block δ-Ni_2Si phase gradually increases while the granular δ-Ni_2Si phase gradually decreases as the Ni content gradually increases (Fig. 2d). This is because when Cu-Ni-Si alloy powders starts to soften and deform under the action of pressure with the increase of sintering temperature and the diffusion of atoms increases gradually, and the adhesion on the surface of the copper, nickel and silicon particles began to alloying reaction. In the process of sintering alloying of driving force mainly comes from the free energy of the atom itself, nickel and silicon can alloying reaction to generate primary phase at grain boundary, as the grow up of the white particles phase, stable saturated, the rest of Ni, Si atoms by atomic diffusion will continue to react in the copper matrix, which form tiny in the grain boundary precipitated phase, and its quantity and distribution is mainly related to the content of Ni and Si . When the mass ratio of Ni to Si is 2:1, 3:1 and 4:1, because of the low content of Ni, it can completely react with Si, and the remaining Si atoms are enriched at the grain boundary (Fig. 2). When the mass ratio of Ni: Si is 5:1, only δ-Ni_2Si was generated in the alloy, and there was significantly less transgranular (Fig. 2d).

Table 1.EDS results of hot-pressed sintered alloys(at%).

Region	Cu	Ni	Si
A	21.04	51.20	27.75
B	86.62	8.60	4.78
C	24.38	10.43	65.19

According to the literature[18] ,the difficulty of forming intermetallic compounds is mainly related to formation enthalpy. However, the enthalpy of mixing of Ni-Si △H(–40kJ/mol) is higher than that of Cu-Si △H(-19kJ/mol) and Cu-Ni △H(4kJ/mol) in Cu-Ni-Si alloy. Therefore, in the process of hot-pressed sintering, Ni and Si preferentially formed a near program structure characterized and eventually evolved into Ni-Si phase.

On the other hand, formation enthalpy can be used to measure the ability of intermetallic compounds to form[19] , and the formation of Ni_xSi_y phase enthalpy formulas can be used (1) to calculate:

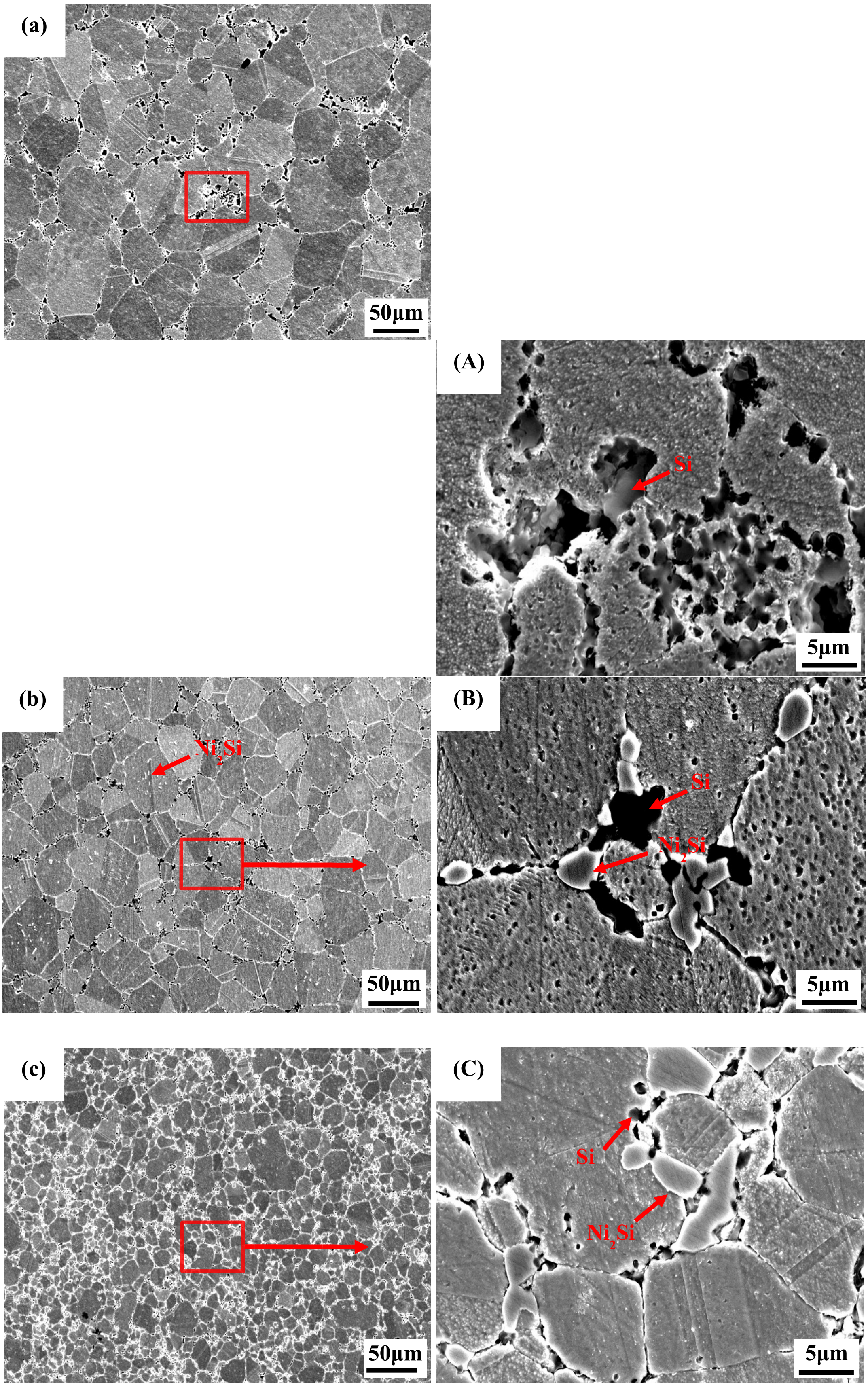
$$\Delta H\left(Ni_x Si_y\right) = \frac{E_{tot}^{NiSi} - xE_{solid}^{Ni} - yE_{solid}^{Si}}{x+y} \quad 1$$

where E_{tot}^{NiSi} is the total energy of an intermetallic compound at equilibrium lattice parameters; E_{solid}^{Ni} and E_{solid}^{Si} are the atomic energy of each element Ni and Si at equilibrium lattice parameters; x is the number of Ni atoms in the unit cell; y is the number of Si atoms in the unit cell. The formation enthalpy of Ni_2Si phase is the lowest calculated by formula (1). It was proved that δ-Ni_2Si phase is more capable of forming than other phases.

The ability to form intermetallic compounds can also be measured by binding energy[20]. The binding strength mainly depends on the absolute value of binding energy, and the higher the absolute value, the higher the binding strength. The binding energy can be calculated by formula (2) :

$$\Delta H\left(Ni_x Si_y\right) = \frac{E_{tot}^{NiSi} - xE_{atom}^{Ni} - yE_{atom}^{Si}}{x+y} \quad 2$$

Where E_{tot}^{NiSi} is the total energy of the alloy phase at the equilibrium lattice constant; E_{atom}^{Ni} and E_{atom}^{Si} are the atomic energy of each element Ni and Si at equilibrium lattice parameters; x is the number of Ni atoms in the unit cell; y is the number of Si atoms in the unit cell. According to the formula (2) calculated the binding energy of the δ-Ni_2Si phase is higher.



(a)
50μm
(A)
Si
5μm
(b)
Ni2Si
50μm
(B)
Si
Ni2Si
5μm
(c)
50μm
(C)
Si
Ni2Si
5μm

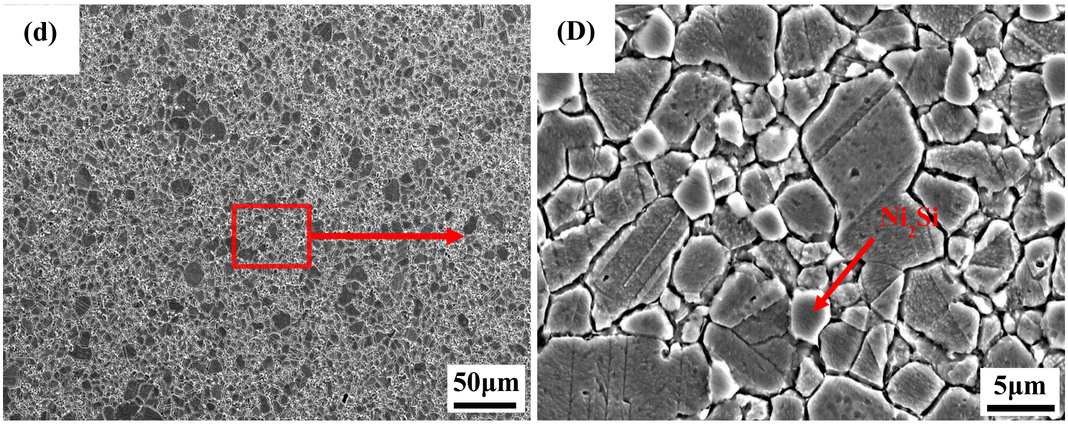


Fig. 3. SEM images of solid solution treatment and the mass ratio of Ni and Si (a)2:1, (b)3:1, (c)4:1, (d)5:1.

Figure 3 shows the microstructure of the alloys after 2h of solution treatment at 900°C. It can be seen from the figure that when the mass ratio of Ni and Si is 2:1, the δ-Ni_2Si phase in the alloy was solid dissolved into the Cu matrix and with only rich Si residue. When the mass ratio of Ni and Si is 3:1, the granular δ-Ni_2Si phase was mostly solid dissolved into the Cu matrix, while the bulk δ-Ni_2Si phase and Si don't change much (Fig. 3b,B). When the mass ratio of Ni and Si is 4:1 and 5:1, the granular δ-Ni_2Si phase was all solid dissolved into the Cu matrix, while the bulk δ-Ni_2Si phase don't change (Fig. 3c, d).

The microstructure of Cu-Ni-Si alloys after ageing treatment is shown in figure 4. As seen from Fig.4(a)-(d), Except the δ-Ni_2Si phase at the grain boundary and there was a smaller second phase was precipitated in the transgranular, according to the XRD analysis of Fig.1(c) , it can be determined that the second phase precipitated is δ-Ni_2Si phase. The size of precipitated phase was smaller than that of hot-pressed sintered, when the Ni and Si mass ratio is 4:1 and 5:1, the number of precipitated phase was larger.

Because of Cu-Ni-Si alloy is a typical solid solution aging reinforced alloy material[21-22], and there are as many as seven kinds of Ni-Si structures[23-28]. These include two Ni_3Si phases (β-Ni_3Si, t-Ni_3Si), one γ-Ni_5Si_2 phase ($Ni_{31}Si_{12}$), two Ni_2Si phases (δ-Ni_2Si, θ-Ni_2Si), one ε-Ni_3Si_2 phase and one o-NiSi phase. According to the first principles, the δ-Ni_2Si phase is the most stable phase with low formation enthalpy[29]. Therefore, δ-Ni_2Si phase was finally formed in the Cu-Ni-Si alloy after heat treatment, which was consistent with the study by Lei et al.[30-31].

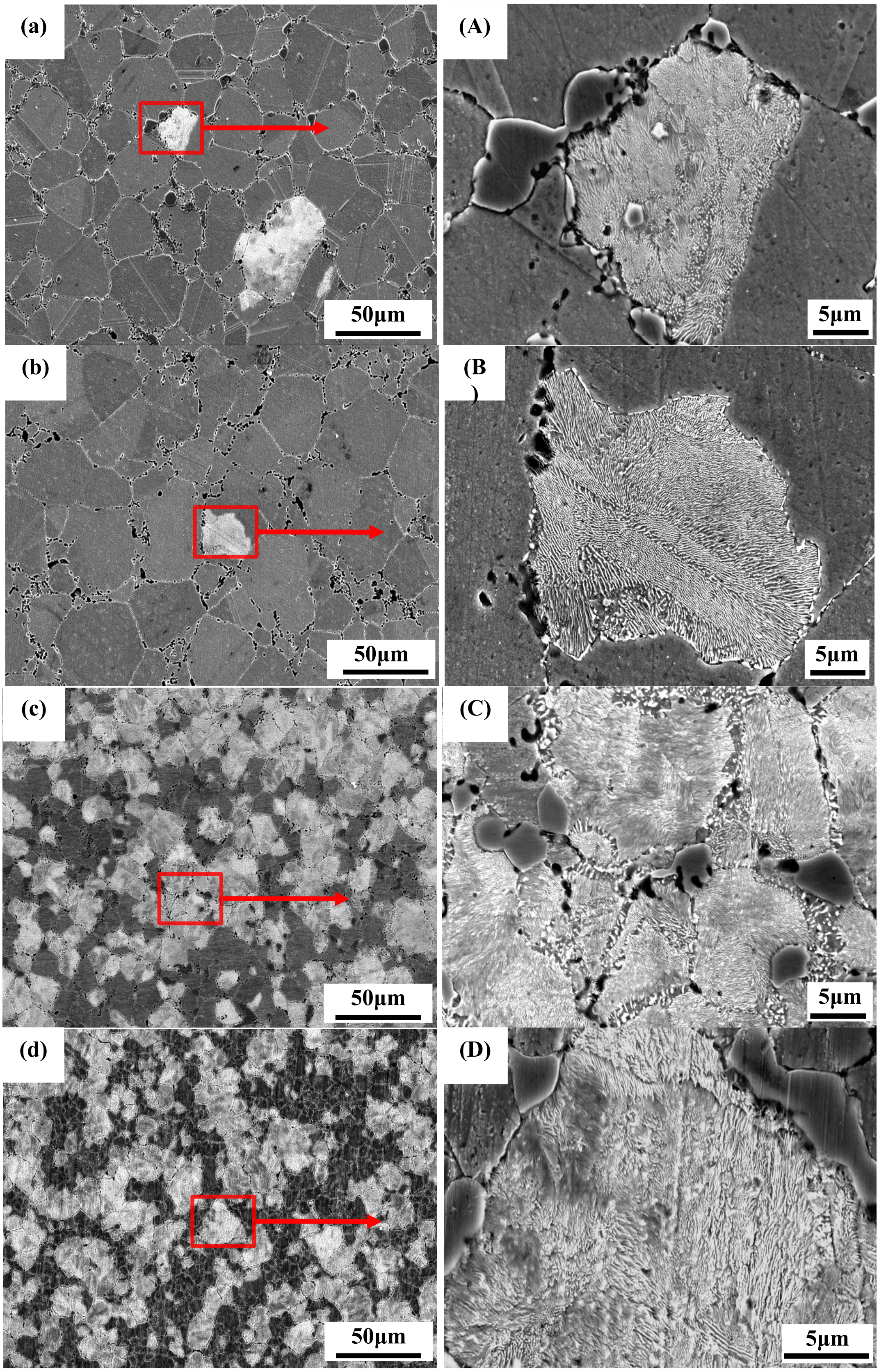


Fig. 4 . SEM images of ageing treatment and the mass ratio of Ni and Si

(a)2:1, (b)3:1, (c)4:1, (d)5:1.

3.2 Electrical and mechanical properties of Cu-Ni-Si alloy

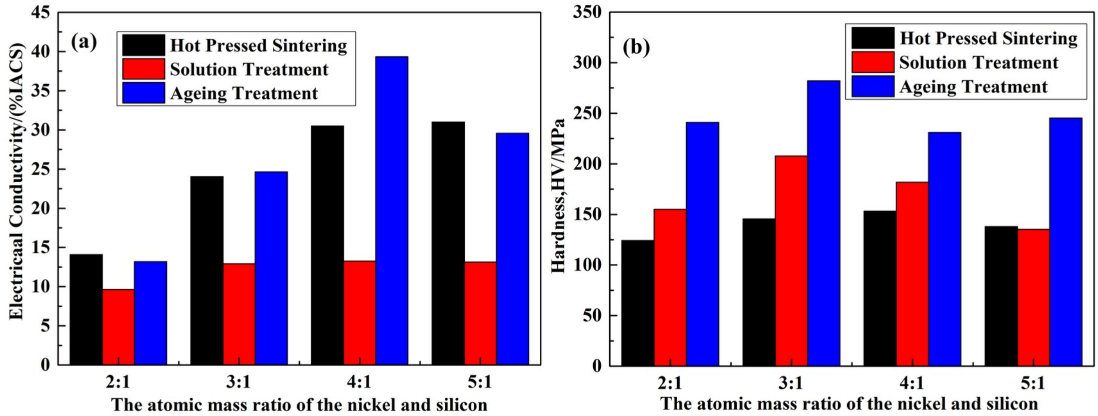


Fig. 5 . Conductivity and vickers hardness of Cu-Ni-Si alloy

The conductivity and vickers hardness of Cu-Ni-Si alloys are shown in figure 5. As seen from Fig. 5(a), after hot-pressed sintered, the electrical conductivity of the alloys increases with the increase of Ni content. While the electrical conductivity of the alloys after solid solution treatment significantly decreases. However, after ageing treatment, the electrical conductivity of the alloys increased with the increase of Ni content, when the mass ratio of Ni and Si was 4:1, the maximum value was 39.33%IACS.

According to literature [34], the electrical conductivity of Cu-Ni-Si alloys are related to the Ni and Si solute atoms in the alloy. When the content of Ni and Si atoms in the Cu matrix are less, the electrical conductivity of the alloy is better. From the microstructure observation in Fig. 2 . It can be seen that when the mass ratio of Ni and Si is less than 4:1, there were obviously surplus Si atoms in the alloy microstructure to form rich Si in the Cu matrix, thus reducing the electrical conductivity of the alloys. After solid solution, a large number of Ni and Si solute atoms were incorporated into the alloys. The scattering effect of solid solution atoms in the matrix on electrons impedes the movement of free electrons. Therefore, the more solid solution atoms in the matrix, the stronger the scattering ability of electrons, and the lower the electrical conductivity of the alloy. However, after aging treatment, Ni and Si atoms in the solid solution of the alloy were precipitated out in the form of δ-Ni_2Si, which purified the matrix of the alloy and greatly improved the electrical conductivity of the alloy.

The vickers hardness of the alloys is shown in Fig. 5(b) . It can be seen from the figure that the vickers hardness of the alloy increases first and then decreases. After ageing treatment, when the mass ratio of Ni and Si is 3:1, the maximum vickers hardness of the alloy is 282.07HV, and when the mass ratio of Ni and Si is 4:1, the minimum vickers hardness of the alloy is 230.95HV. This is because the δ-Ni_2Si phase precipitated after aging treatment can effectively prevent dislocation and grain boundary sliding, thus increasing the hardness of the alloy. And it can be concluded that Cu-Ni-Si alloys with 4h aging has the best comprehensive performance when the mass ratio of Ni and Si is 4:1.

4. Conclusions

1 There were no Ni-Si intermetallic compounds except the δ-Ni_2Si phase in the Cu-Ni-Si alloys prepared by powder metallurgy method, and the δ-Ni_2Si phase is more evenly distributed and smaller in size.

2 After ageing treatment, when the mass ratio of Ni and Si was 2:1 and 3:1, a little granular δ-Ni_2Si phase was precipitated. When the mass ratio of Ni and Si was 4:1 and 5:1, the number of granular δ-Ni_2Si phase increased significantly.

3 The electrical conductivity and vickers hardness of the alloys with four components in different states were tested. After ageing treatment, when the mass ratio of Ni and Si is 4:1, both the electrical conductivity and vickers hardness of the alloys were greatly improved. The electrical conductivity was 39.33%IACS and vickers hardness was 230.95HV, At this point Cu-Ni-Si alloys has the best comprehensive performance.

Acknowledgments

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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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