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Thermomechanical treatment of super high strength Cu-8.0Ni-1.8Si alloy

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Abstract: The microstructures and properties of Cu-8.0Ni-1.8Si alloy subjected to different heat treatments were examined by mechanical and electrical properties measurements, optical and transmission electron microscopes observation. The results show that the precipitation process during aging can be accelerated by the cold deforming before aging. As the Cu-8.0Ni-1.8Si alloy is subjected to solution treatment at 970 ℃ for 4 h, cold rolling to 60% reduction, and then aging at 450 ℃ for 60 min, its properties are σ_b=1 050 MPa, $\sigma_{0.2}$=786 MPa, δ=3.2% and conductivity 27.9%(IACS). The strengthening mechanisms of the alloy include spinodal decomposition strengthening, ordering strengthening and precipitation strengthening. The precipitation of the alloy is nano-scale Ni_2Si phase.

Key words: Cu-8.0Ni-1.8Si alloy; thermomechanical treatment; spinodal decomposition; ordering

1 Introduction

The CuNiSi alloy is an age-hardening copper alloy owning both high strength and electrical conductivity [1−2]; these properties are attributed to the precipitation of δ-Ni_2Si phase from the supersaturated solid solution of the alloy during aging[3−4]. The CuNiSi alloys with low solute atoms (the quality content of Ni and Si atoms in general are less than 3.5% and 0.75%, respectively) have been studies in detail[5−6]. However, little extensive investigation paying attention to the alloy with high solution atoms has been made. With the increase of solution atoms, the strength of the alloy increases rapidly, and a suitable conductivity is obtained at the same time [7−8]. It has an extensive application prospect in spring materials to replace the Be-bronze. In this paper, Cu-8.0Ni-1.8Si alloy has been developed, the content of Ni and Si are increased to 8.0% and 1.8% respectively, the structural transition of the alloy and its properties during thermomechanical treatment have been investigated.

2 Experimental

The Cu-8.0Ni-1.8Si alloy was induction melted, cast into flat ingots and then homogenized at 950 ℃ for 24 h and finally rolled to 3 mm thickness plate. The thermomechanical treatments are divided into two processes and are expressed as follows:

Process I: Solution at 970 ℃ for 4 h and then water quench-aging at 450 ℃ for different times (ST+aging).

Process II: Solution at 970℃ for 4h and then water quench-cold rolling to 60% reduction-aging at 450 ℃ for different times) (CR+aging).

The microhardness of the sample was measured at a load of 3 N with a holding time of 15 s on a Vickers hardness machine. The specimen was mechanically polished to 0.07 mm and then jet electro-polished in a mixing solution of CH_3OH and HNO_3 with volume ratio of 1:2. The transmission electron microscope observation was conducted on FEI Tecnai G^{2}20, and the operation voltage was 200 kV.

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3 Experimental results

3.1 Effect of Process I on alloy hardness and conductivity

The properties of CuNiSi alloy can be affected by many factors, which mainly include aging temperature, aged time and pre-cold deformation before aging[9−11].

The microhardness evolution of the alloy solution-treated at 970 ℃ for 4 h, water quenched and then aged at 450 ℃ for different times is shown in Fig.1. The hardness of the alloy increases quickly with the increase of aging time, the hardness approaches to the maximum (HV271) when aged for 2 h, then decreases.

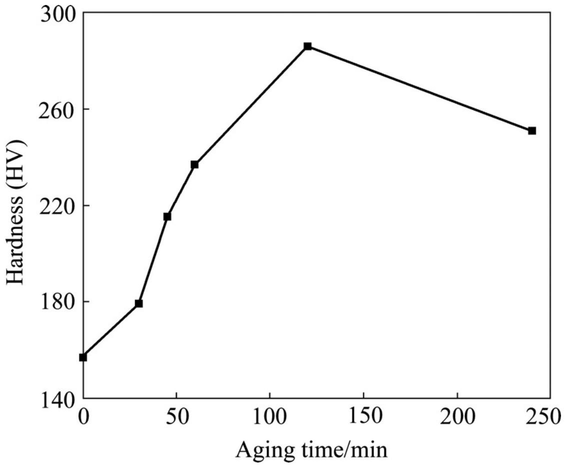

Fig.1 Evolution of hardness with aging time under process Ⅰ

The conductivity change of the alloy treated by the process as mentioned above is shown in Fig.2. It can be seen from Fig.2 that, the conductivity of alloy increases continually with the increase of aging time.

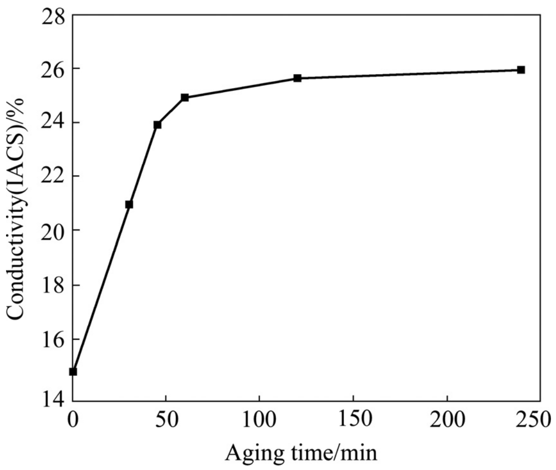

Fig.2 Change of conductivity with aging time under process Ⅰ

3.2 Effect of Process Ⅱ on alloy properties

The hardness evolution of the alloy solution-treated at 970 ℃ for 4 h, water quenched and cold rolled to 60% reduction then aged at 450 ℃ for different times is shown in Fig.3. From Fig.3, only aged for 1 h, the hardness increases to the maximum, HV333, then with the increase of aging time the hardness decreases. The tensile properties of the alloy treated by this process are measured to be σ_b=1 050 MPa, $\sigma_{0.2}$=786 MPa and δ= 3.2%.

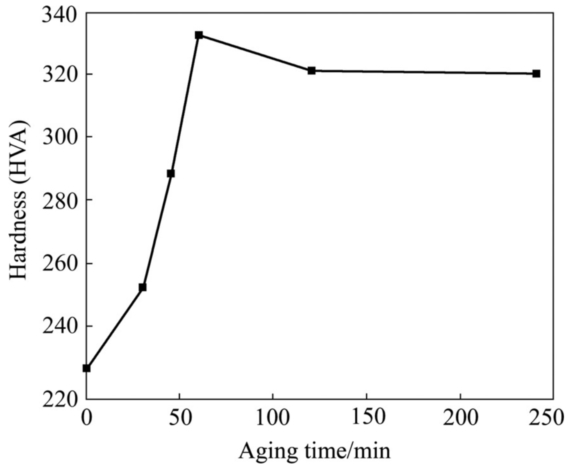

Fig.3 Evolution of hardness with aging time under process Ⅱ

The conductivity transition of the alloy solution-treated at 970 ℃ for 4 h, water quenched and cold rolled to 60% reduction then aged at 450 ℃ for different times is shown in Fig.4. The conductivity increases rapidly when the aging time is lower than 1 h, and increases slowly with prolonging the aging time. When aged for 1 h, the conductivity(IACS) is 27.9%.

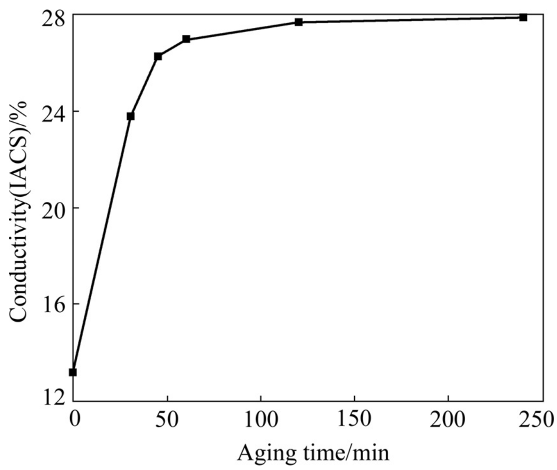

Fig.4 Change of conductivity with aging time under process Ⅱ

3.3 TEM analysis

The electron micrographs and electron diffraction patterns of CuNiSi alloy solution-treated at 970 ℃ for 4 h, water quenched and cold rolled to 60% reduction then aged at 450 ℃ for 60 min is shown in Fig.5. Figs.5(a), (c) and (e) show the TEM bright field images in different fields and their corresponding electron diffraction patterns

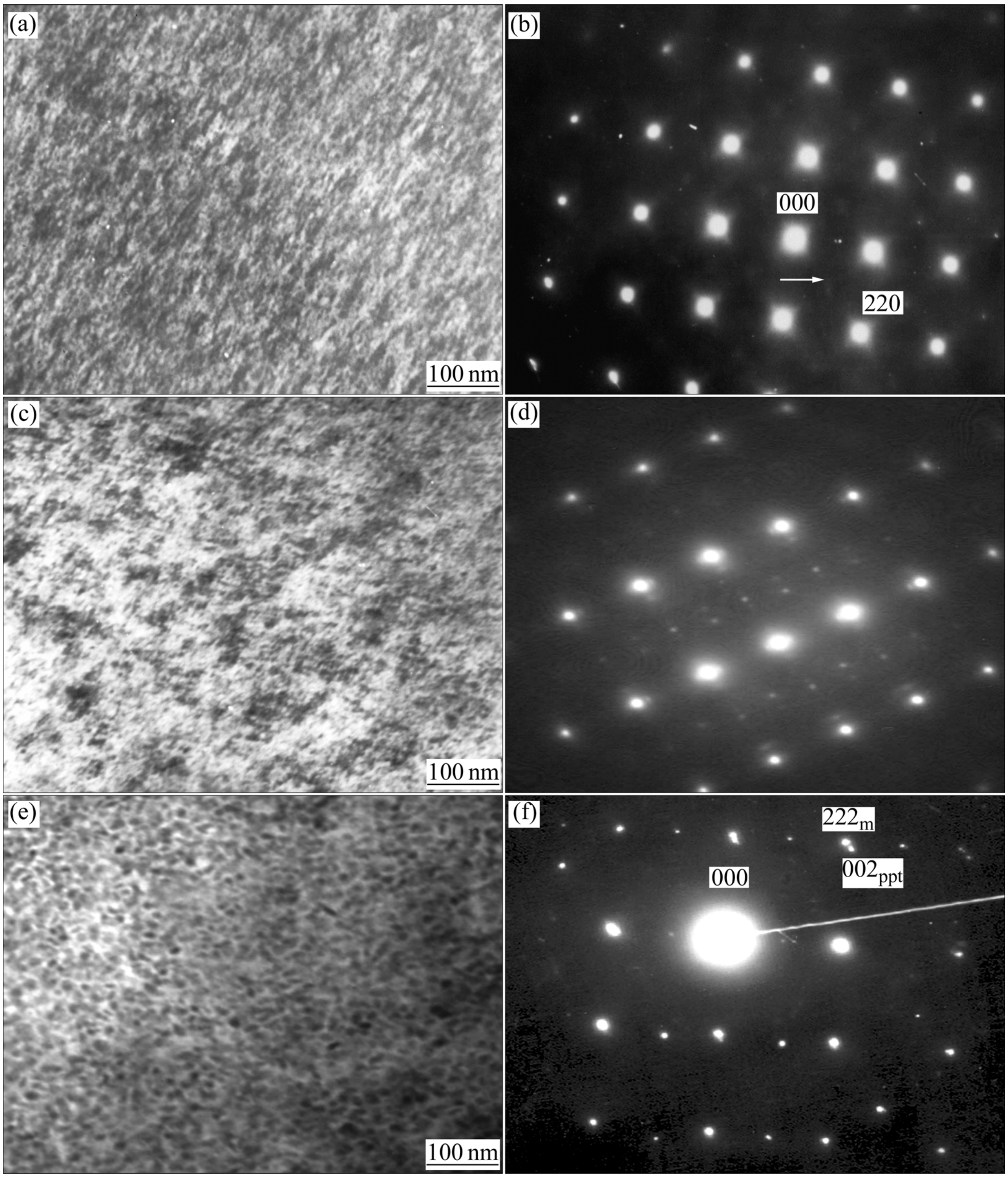

Fig.5 TEM images of CuNiSi alloy treated by processing Ⅱ and corresponding diffraction electron pattern: (a), (c), (e) BF images of CuNiSi alloy aged at 450 ℃ for 60 min; (b) Diffraction pattern for Fig.5(a); (d) Diffraction pattern for Fig.5(c); (f) Diffraction pattern for Fig.5(e)

are shown in Figs.5(b), (d) and (f), respectively. Fig.5(a) shows a discontinuous precipitation colony, the satellites of modulation can be clearly seen from Fig.5(b) (corresponding to electron diffraction pattern of Fig.5(a)), which demonstrates the subsistence of structure modulation in the specimen[12−13]. The {011} superlattice reflection can be seen in Fig.5(d) (corresponding to electron diffraction pattern of Fig.5(a)), which suggests that DO_{22} order structure occurs[14]. From Fig.5(e) the non-scale precipitation can be seen, its selected diffraction is shown in Fig.5(f), which indicates that the precipitations are Ni_2Si, the crystallographical relationship of the Ni_2Si phase and the parent phase is $(110)_{\alpha\text{-Cu}}//(001)_{Ni_2Si}, [001]_{\alpha\text{-Cu}}//(010)_{Ni_2Si}$.

4 Discussion

The phenomenon of coexistence of spinodal decomposition and ordering has been found in many alloys with continuous phase transition, such as Ni-Ti, Cu-Ti[15−16]. The phenomenon of coexistence of spinodal decomposition and ordering in CuNiSi alloys has also been found[13−14]. ZHAO et al[13] have observed this phenomenon by TEM, X-ray diffraction and other means. DONG et al[14] have explained the coexistence of phenomenon of spinodal decomposition and ordering in CuNiSi alloys with non-continuous phase transition by constructing thermodynamical graphics. They have further explained that Ni and Cu fully solve mutually in solid state, as the content of Ni is from 30% to 96% (mass fraction). A region of metastable decomposition exists below 322 ℃. Addition of Fe, Cr, Sn, Ti, Si to the alloy can significantly shift this region. The phenomenon of coexistence of spinodal decomposition and ordering has also been found in the tested alloy aged at 450 ℃ for 60 min, the precipitation of Ni_2Si phase can be seen too. The peak hardness of the alloy can reach about HV333 under processing Ⅱ, which is due to the spinodal decomposition strengthening, second phase particle precipitation strengthening and ordering strengthening.

The spinodal decomposition in alloy occurs, the solute enrichment zones and depleted zones can be continuously formed, the formation of solute enrichment zones and depleted zones will affect the alloy strength. The increase of yield strength can be expressed as follows[17]:

$$\Delta\sigma_s = \frac{6\mu(r\cdot f)^{1/2}\varepsilon^{3/2}}{b} \tag{1}$$

where μ is the shear modulus of precipitated particles; r is the radius of precipitated particles, the radius of solute enrichment zones in spinodal decomposition organization is 1/2 of spinodal wavelength; f is the volume fraction of precipitated particles; ε is the mismatch function; b is the Burger's vector of copper matrix.

It can be estimated that the alloy strengthening enhanced by ordering is as follows[18]:

$$\tau = \frac{KS^3}{b^2a^3}\left(\frac{T_c^3 f r_s}{G}\right)^{1/2} \tag{2}$$

where K is Boltzmann constant; T_c is the ordering phase transition temperature; S is the degree of order; f is the volume fraction of ordering phase; r_s is the radius of ordering phase being sheared; a is the lattice constant.

The structure of Ni_2Si is complex orthogonal, the particles are hardly sheared by dislocation, and the dislocation only bypasses it. The increase of yield stress by the nano-scale Ni_2Si precipitations can be described by Orowan mechanism, the increment $\Delta\sigma_{Orowan}$[19] is as follows:

$$\Delta\sigma_{Orowan} = \frac{0.81MGb}{2\pi(1-\nu)^{1/2}}\frac{\ln(d_p/b)}{(\lambda-d_p)} \tag{3}$$

$$\lambda = \frac{1}{2}d_p\sqrt{\frac{3\pi}{2f_v}} \tag{4}$$

where M is Taylor-factor (M of Cu is 3.1); G is the shear modulus of matrix (the shear modulus of Cu is 45.5 GPa); ν is the Poisson's ratio (=0.34); b is the Burgers vector (=0.255 nm); λ is the average particle plane square lattice spacing (that is apparent particle spacing); d_p is the average particle diameter; f_v is the volume fraction of particle.

After aging for a longer time at 450 ℃, the strength of experimental alloy decreases, which is due to the growth of precipitation particles. The typical morphology of the alloy aged at 450 ℃ for 128 h is shown in Fig.6, the precipitation particles coarsen obviously.

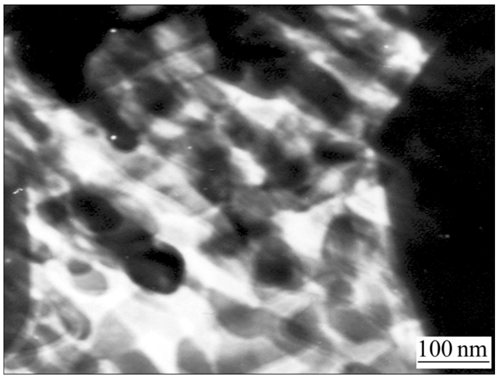

Fig.6 TEM image of CuNiSi alloy aged at 450 ℃ for 128 h

5 Conclusions

1) The strengthening mechanisms of Cu-8.0Ni-1.8Si alloy solution-treated at 950 ℃ for 4 h, water quenched and cold rolled to 60% reduction then aged at 450 ℃ for 60 min include spinodal decomposition strengthening, precipitation strengthening and ordering strengthening; the precipitation phase in the alloy is nano-scale Ni_2Si phase.

2) Cu-8.0Ni-1.8Si alloy is subjected to solution treatment at 970 ℃ for 4 h, cold rolled to 60% reduction, and then aged at 450 ℃ for 60 min, its properties are that σ_b is 1 050 MPa, $\sigma_{0.2}$ is 786 MPa, δ is 3.2% and conductivity is 27.9%(IACS).

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