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Effects of Cr and Zr additions on microstructure and properties of Cu-Ni-Si alloys

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ABSTRACT

Cu-Ni-Si alloys are widely used for electrical applications owing to high strength and high electrical conductivity. In this work, the effects of Cr and Zr additions on microstructure and properties of Cu-Ni-Si alloys were investigated. The addition of Cr and Zr results in formation of Cr_3Si and Ni_2SiZr intermetallic compounds, respectively, thus increases the electrical conductivity of Cu-Ni-Si alloy and refines the microstructure. Microstructure analysis confirms the presence of δ-Ni_2Si precipitates, which strengthens the alloy through Orowan mechanism. Alloying with Zr element deteriorates the mechanical property of Cu-Ni-Si alloy, whereas in the presence of Cr, to the contrary, the ultimate tensile strength is increased, whether Zr is incorporated or not. Moreover, the addition of Zr can decrease the stacking fault energy (SFE) and promote formation of deformation twins. The best integrated performance is obtained through co-addition of Cr and Zr elements. The ultimate strength, elongation and electrical conductivity are 706 MPa, 9.5% and 48.2% IACS, respectively. The precipitation kinetics was discussed in terms of Avrami equation and the activation energy of Ni_2Si precipitation was obtained. The calculated activation energies of precipitation are 105, 89, 115 and 111 kJ/mol for Cu-Ni-Si, Cu-Ni-Si-Zr, Cu-Ni-Si-Cr and Cu-Ni-Si-Cr-Zr alloy, respectively.

1. Introduction

Copper alloys exhibiting both high strength and high electrical conductivity are widely used for electrical applications, such as lead frames, railway contact wires and connectors [1–3]. Various copper alloys have been developed to meet industrial demands, such as Cu-Be [4], Cu-Cr [5–7], Cu-Fe-P [8], Cu-Ni-Si [9–11] and Cu-Mg [12] alloys. Of all the copper based alloy systems, precipitation strengthened Cu-Ni-Si system alloys have attracted much attention due to their ultrahigh strength and high electrical conductivity. The formation of Ni-Si precipitates in copper matrix increases the strength with minimum decrease in electrical conductivity [13]. Despite applications in electrical industry, the Cu-Ni-Si system alloys are also used as resistance welding electrodes and molding tolls, and are the preferred candidate material for the first wall of nuclear reactor [14,15].

In recent decades, attempts have been made to further improve the strength of Cu-Ni-Si alloys and addition of trace amount of alloying elements appears to be an effective way. Addition of Co element can form orthorhombic (Ni, Co)$_2$Si precipitates sharing the same crystal system with Ni_2Si precipitates and decrease the inner-precipitate spacing as well as dislocation density [16,17]. Trace amount of P can suppress the discontinuous precipitation reaction, resulting in enhancement of both strength and elongation [18]. Adding Cr to a Cu-Ni-Si-P alloy decreases the grain size greatly [18]. V addition suppresses the recrystallization, retards the grain growth, and accelerates the precipitation of Ni_2Si metallic compounds [19]. The addition of trace Ti reduces grain size and greatly increases elongation. In addition, the equilibrium concentration of Ni_2Si in copper matrix is reduced and precipitation is accelerated by trace Ti [20].

Due to the low solubility of Cr and Zr in copper, Cu-Cr and Cu-Zr alloys are capable of preserving high electric conductivity [7,21]. Some of recent reports pointed out that Zr lowers the stacking fault energy in copper and thus contributes to higher work hardening [22,23]. In this study, trace amount of Cr and Zr additions were added to a Cu-2.0 wt%Ni-0.5 wt%Si alloy for the sake of

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Table 1
Designed and tested chemical compositions of Cu-Ni-Si alloys with Cr and Zr additions.

Alloys	Designed					Tested				
	Ni	Si	Cr	Zr	Cu	Ni	Si	Cr	Zr	Cu
CuNiSi	2	0.5	–	–	Bal.	1.9168	0.5226	/	/	Bal.
CuNiSiZr	2	0.5	–	0.15	Bal.	1.8670	0.4726	/	0.1608	Bal.
CuNiSiCr	2	0.5	0.3	–	Bal.	1.8275	0.4881	0.3957	/	Bal.
CuNiSiCrZr	2	0.5	0.15	0.15	Bal.	1.8794	0.5995	0.2158	0.2482	Bal.

improving mechanical property while maintaining electrical conductivity.

2. Experimental

Ingots of Cu-2.0 wt%Ni-0.5 wt%Si alloys with Cr and Zr additions were prepared by induction melting in a graphite furnace under argon atmosphere. The designed and tested chemical compositions are listed in Table 1. The ingots were casted at 1523 K in a quasi-cubic iron mold, homogenized at 1233 K for 24 h and hot-rolled with 66% reduction in thickness at 1123 K. The hot rolled sheets were solution treated at 1233 K for 1 h and quenched in water before cold rolled with 60% reduction at room temperature. These rolled plates were then isochronally aged for 1 h at various temperatures and isothermally aged at 723 K and 773 K for various time. As for tensile test, the rolled plates were pre-aged at 723 K for 1 h, cold rolled with 50% reduction and finally aged at 648 K for 8 h.

Microhardness tests were performed using Vickers method on a MH-50 type microhardness tester. The indentations were made with a diamond square-based pyramid under a load of 0.2 kg for 10 s dwelling time on well polished surface of samples. The test was repeated 5 times for each sample to obtain an arithmetic average value. For the electrical conductivity, a D60K digital electrical instrument was applied at 293 K and the results are presented by International annealed copper standard (IACS). The microstructures were observed using a JSM-5600LV type of scanning electronic microscopy (SEM) and an Olympus GX51 type of optical microscopy (OM). The samples were prepared by conventional mechanical polishing method and etched in an aqueous solution containing 3 g $FeCl_3$ + 95 ml C_2H_5OH + 2 ml HCl. Transmission electron microscope (TEM) samples were obtained by double jet electrolytic-polishing at −30 °C within a bath containing 30% nitric acid and 70% methanol. The resulting foil specimens were observed under Talos F200× microscope with an acceleration voltage of 200 kV. The synchrotron X-ray radiation analysis was performed at 4B9A beamline of Beijing Synchrotron Radiation Facility (BSRF). The samples were illuminated with a monochromatic X-ray beam at an energy of 8050 eV (λ = 1.54 nm) to acquire an accurate measurement.

3. Results and discussions

3.1. Microstructure

3.1.1. Microstructure changes during thermomechanical treatment

Fig. 1 shows the optical macrostructures of as cast designed Cu-Ni-Si-(Cr-Zr) alloys. Large grains whose size exceeds several micrometers are observed in all cases owing to the low cooling speed of iron mold surrounded by sands. For raw Cu-Ni-Si alloys, typical

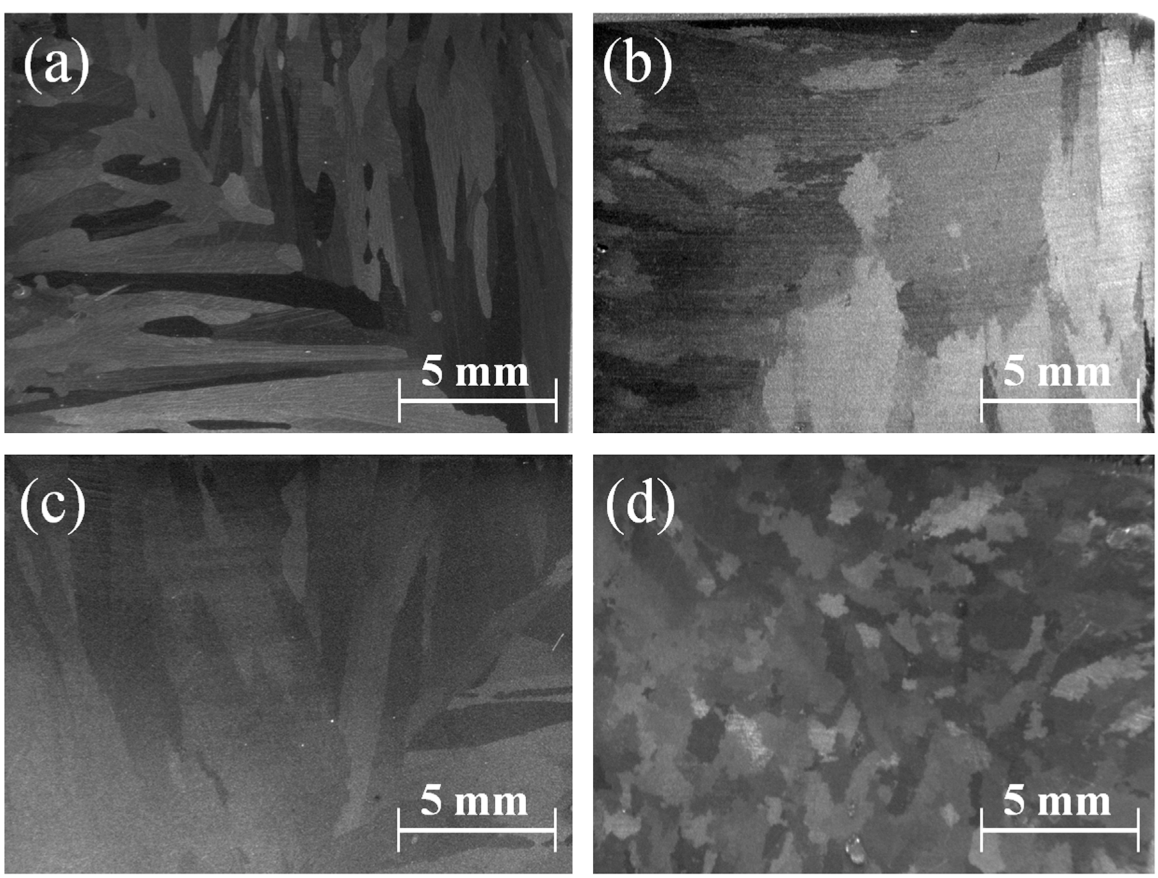

Fig. 1. Optical macrostructures of as cast Cu-Ni-Si alloys: (a) Cu-Ni-Si alloy; (b) Cu-Ni-Si-Zr alloy; (c) Cu-Ni-Si-Cr alloy; (d) Cu-Ni-Si-Cr-Zr alloy.