Annealing effect of micro-alloying on the microstructure and properties of Cu-10Zn alloy

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Abstract. The effect of Fe and P (Ni and Si) on the microstructure and properties of Cu-10Zn alloys has been investigated using hardness test, electrical conductivity measurement, optical microscopy and transmission electron microscopy. γ-Fe precipitates formed during the aging process, but there is almost no effect of precipitation strengthening on the Cu-Zn-Fe-P alloy and sparsely Fe3P precipitates existed in the matrix. After homogenization treatment at 900 °C for 2h, hot rolling by 80%, cold rolling by 80%, and ageing treatment at 400 °C for 30min, Cu-Zn-Ni-Si alloy obtained good combinations of hardness (219.8HV) and electrical conductivity (28.2%IACS). Ni2Si precipitates formed during aging process and the crystal orientation relationship between matrix and precipitates is: (200)α || (100), γ || [100], (101)γ || [010]. Compared with Cu-Zn-Fe-P, Cu-Zn-Ni-Si has finer grains, and the precipitation strengthening effect is more obvious.

1 Introduction

Cu-Zn alloys are a typical solid solution strengthening copper alloy [1]. They have been widely used for industrial products, such as connectors, valves, pipes, radiators and so on, due to its good electrical conductivity, thermal conductivity, low cost and easy to manufacture [2-3]. However its low performance limited their application. With the rapid development of the machinery manufacturing industry, its corresponding performance requirements are also increasing [4-5]. In the past few years, many researchers have made great efforts to take micro-alloying, deformation and heat treatment to improve the strength, conductivity and softening resistance of the copper-based alloys [5-6]. But there are few reports on the effect of performance of Cu-Zn alloys can be found that most previous studies were focused on their deformation [7-8]. It found that the comprehensive performance of the alloy can be obviously improved by codoping Fe/P or Ni/Si in the copper matrix. Thus the same effect is expected to obtained in Cu-Zn matrix. In this paper, Cu-Zn-Fe-P (Ni-Si) alloys have been designed and investigated, with an aim to reveal the effect of micro-alloying on the microstructure and properties of Cu-Zn alloys in detail to explore a new strategy to develop new complex brass alloys.

2 Materials and experimental procedure

Electrolytic copper, pure zinc, pure nickel, pure silicon, and pure ferrum were prepared and melted in a intermediate frequency furnace, and then cast in an iron mold. After surface defects were removed, all the casting ingots were homogenized at 900°C for 2h, then rapidly hot rolled from a thickness of 30mm to 5mm, followed by quickly quenching into cold water. The hot-rolled plate was planed on both sides to remove surface defects, and then cut into small samples. Samples were cold rolled with 80% reduction at room temperature, followed by isothermal aging at different temperatures for various time in a salt-bath furnace.

Vickers hardness (HV) was carried out on HV-5 type microhardness tester with 1-2 kg load and 10 s loading time according to ASTM E384-11 Standard [9]. Electrical conductivity was measured at 20°C using a Eddy Conductivity Instrument, taking the average of 7 values to minimize errors. The specimens were etched in a solution containing FeCl3, hydrochloric acid and alcohol and optical observations were made on a Leica optical microscope. Transmission electron microscopy (TEM) samples were prepared by double jet electropolishing techniques using a 20% nitric acid in methanol solution at about -35°C. TEM observations were carried out on a TECNAI G2 F20 transmission electron microscope with operation voltage of 200 kV.

3 Results and discussion

3.1. Thermo-mechanical treatment
The OM images of as-cast alloy are shown in Fig.1. As shown in Fig.1a, it shows that Cu-Zn-Fe-P alloy is mainly composed of α-Cu matrix, faint dendrites in the grains can be found and the average grain size is about 550μm. Fig.1b shows the OM image of Cu-Zn-Ni-Si, lots of dendrites appeared amongst the grains and the average grain size of the alloy is only about 260μm indicating the grains of as-cast Cu-Zn alloy can be effectively refined with addition of Ni and Si.

**3.2. Effect of small alloying additions on hardness and resistivity of the alloy during aging treatment**

The hot rolled-quenched and cold rolled samples were aged at different temperatures for various time in a salt-bath furnace. Fig.2 shows the variation of hardness and electrical conductivity of Cu-Zn-Fe-P alloys after ageing treatment at 200°C, 250°C, 300°C and 350°C. The hardness of Cu-Zn-Fe-P increased more slowly as aging treatment below 300°C with duration, but it decreased rapidly with aging time when the aging temperature was above 300°C. These results were very similar to that of Cu-Zn alloy. The corresponding electrical conductivities increased continuously and more and more rapidly with the aging temperature raised which was different from that of Cu-Zn alloy. Hence it can be inferred that some precipitation are produced during the aging process.

![Figure 1. Optical microstructure of designed alloys. (a)as-cast Cu-Zn-Fe-P alloy; (b)as-cast Cu-Zn-Ni-Si alloy](Image)

![Figure 2. Variation of hardness and electrical conductivity of Cu-Zn-Fe-P alloys during aging treatment: (a) hardness ;(b) electrical conductivity](Image)

Fig.3 shows the variation of hardness and electrical conductivity of Cu-Zn-Ni-Si alloys after ageing treatment at 350°C, 400°C, 450°C and 500°C. The higher the aging temperature is, the lower the peak hardness value of the alloy reaches, and the peak aging time occurs. The electrical conductivity increased with aging time at different temperature. The electrical conductivity raised more rapidly at the initial stage with aging temperature rising. The peak hardness values of Cu-Zn-Ni-Si alloys were 224.5HV, 219.8HV, 215.2HV, 209.3HV as aging treatment at 350°C for 120 min, 400°C for 30 min, 450°C for 5 min and 500°C for 1 min respectively. And the corresponding electrical conductivities were 26.9%IACS, 28.2%IACS, 25.7%IACS and 25.2%IACS, respectively.
4 Discussion

Cu-Fe binary alloy phase diagram shows that the solubility of Fe in Copper decreases with the temperature down (3.5% at 1050°C, 1.4% at 900°C and only 0.0004% blow 300°C). While the temperature decreasing to a certain extent, γ-Fe can precipitate out from the supersaturated solid solution which can strengthen the alloys. Fig.4 shows TEM micrographs, corresponding energy dispersive X-ray spectrometry (EDS) and selected-area diffraction patterns (SADP) of cold rolled Cu-Zn-Fe-P alloy aged at 450°C for 10h. The TEM bright-field (BF) micrograph and the corresponding SADP of the Cu-Zn-Fe-P sample with electron beam parallel to [110]α was shown in Fig.5a. Nanoscale γ-Fe particles with horseshoe-shaped strain-field contrast are dispersed in the sample. This indicates that the γ-Fe precipitates are coherent with the matrix and the length of zero-contrast line is less than 2nm. There is no second phase diffraction spots can be found that only copper matrix diffraction spots exist. This mainly because both Cu and γ-Fe have face center cubic structure with structure parameters a=0.3615nm and a’=0.3590 nm respectively, and the lattice misfit of them is only 0.7% [10]. Thus the SPAD of γ-Fe would be coincident with that of copper due to this fully coherent effects.

On the basis of the above hardness curve, it reveals that γ-Fe precipitated out from Cu-Zn-Fe-P alloy during aging treatment, but the hardening effect was very faint. Solute segregation to dislocation, analogous to the formation of Cottrell atmospheres in interstitial solid solutions, was primarily responsible for anneal hardening phenomenon of the Cu-Zn alloy [11]. While the precipitation strengthen by coherent γ-Fe precipitates was the main strengthening mechanism to Cu-Zn-Fe-P alloy. As for the electrical conductivity of Cu-Zn-Fe-P alloy, it was highly increased due to the precipitation of γ-Fe, especially at high temperature (above 300°C). As we known, alloy softening occurs at high temperatures is primarily due to two reasons as follow. One is the size of precipitates increased with the aging time that make the precipitation strengthening effect down, the other is the soft effect of recovery and recrystallization. As seen from the hardness curves of Cu-Zn-Fe-P alloy above, the precipitation strengthening of Cu-Zn alloy with addition of iron and phosphorus is very tiny that is even less than the soft effect of recovery and recrystallization.

TEM micrographs and selected-area diffraction
patterns with electron beam parallel to [001]_\alpha of cold rolled Cu-Zn-Ni-Si alloy aged at 400°C for 16h are shown in Fig.5.

![Figure 5. TEM micrographs and SADPs of Cu-Zn-Ni-Si alloys that under ageing treatment at 400°C for 16h: (a) bright-field micrograph; (b) beam direction of SADP along [001]_\alpha](image)

With the aging at 400°C for 16h, great deals of rod-shaped and disc-shaped precipitates were found in the bright-field of Cu-Zn-Ni-Si alloy as shown in Fig. 5a. The corresponding SADP with electron beam parallel to [100]_\alpha of the Fig. 6b was shown in Fig. 5b.

The rod-shaped precipitates mainly have two directions perpendicular to each other, while the disc-shaped precipitates seem to be embedded in the matrix. The diffraction spots from δ-Ni2Si precipitates appeared clearly, and the indexation result indicated that the crystal orientation relationship between matrix and δ-Ni2Si precipitates is (001)m∥(001)p, [110]m∥[100]p.

On the basis of the foregoing, it appears that Cu-Zn-Ni-Si alloy has a pronounced aging response, and good combinations of hardness and electrical conductivity can be obtained under aging treatment at 400°C for 30min. This demonstrates the precipitation strengthening effect of addition of Ni and Si is more valid and effective contrast to addition of Fe and P.

5 Conclusions

1. Solute segregation to dislocation was primarily responsible for anneal hardening phenomenon of the Cu-Zn alloy. The addition of iron and phosphorus cannot refine the grains of Cu-Zn alloy effectively. γ-Fe precipitates formed in the Cu-Zn-Fe-P alloy during the aging process, but very week effect of precipitation strengthening on the alloy can be obtained.

2. The addition of nickel and silicon refines the grains of Cu-Zn alloy effectively. δ-Ni2SiSi precipitates formed in the Cu-Zn-Ni-Si alloy during aging treatment which can make strongly precipitation strengthening effect. The crystal orientation relationship between the matrix and precipitates is: (001)m∥(001)p, [110]m∥[100]p.

3. After homogenization treatment at 900°C for 2h, hot rolling by 80%, cold rolling by 80%, and ageing treatment at 400°C for 30min, Cu-Zn-Ni-Si alloy obtained good combinations of hardness (219.8HV) and electrical conductivity (28.2%IACS).

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