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**Enhanced mechanical strength of Cu–Sn alloy by Mg addition**

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**Abstract**

In recent years, the commercially available Cu–Sn alloy has attracted great interest within the new energy vehicles and industrial robots industries because of its relatively excellent comprehensive performance as compared to those of Cu–Ag and Cu–Mg alloys. In this work, we study the possibility of improving the tensile strength of Cu–Sn alloy via Mg addition. Our results show that, the addition of Mg could significantly improve the strength of the Cu–Sn alloy, the tensile strength of the Cu–Sn alloy was increased from 399MPa to 427MPa by 0.02 wt.% Mg addition after 80% cold-rolled reduction. This can be ascribed to the combined effect of the acceleration of the grain refinement and the promotion of the sub-structures formation by Mg addition during cold rolling process. Larger number density and more uniformly distributed sub-structures with an average size of 120 nm were formed in Mg-contained alloy than that in Mg-free alloy after 80% reduction. However, the Mg addition slightly decreased the electrical conductivity (EC) of the alloy (1.5%IACS), because of the lattice distortion caused by Mg atoms.

1. Introduction

Recently, with the rapid development of new energy vehicles, medical devices and industrial robots, high mechanical strength and high electrical conductivity (EC) copper alloy wire conductors have become more and more desired [1–5]. Conventionally, the copper alloy wire conductors are mainly made of Cu–Ag, Cu–Sn and Cu–Mg alloys. In comparison with the Cu–Ag and Cu–Mg alloys, Cu–Sn alloys have the advantages such as simple production process, high finish product rate, costless, and relatively high electrical conductivity. However, the application of Cu–Sn alloy wire conductors is limited by its relatively low strength.

Numerous reports have been demonstrated that the mechanical strength of the Cu alloys can be significantly enhanced by the addition of Mg element [6–9]. Monzen and Watanabe [10] found that when 0.1wt. % Mg was added in Cu–2.0 Ni–0.5 Si (wt.%) alloy, the formation of disk–shaped Ni3Si precipitates was promoted, and the inter–precipitate spacing was reduced, which resulted in the improvement of the mechanical properties. Sun et al. [11] investigated the influence of the addition of Mg on the microstructure and softening resistance of Cu–Cr alloys. They found that, during annealing, the Mg atoms were diffused out from the Cr precipitates and segregated between the Cr precipitate and matrix interface, which plays an important role on refining the Cr precipitates, and leading to a higher tensile strength in the Mg-contained Cu–Cr alloy. However, it is obviously found that these studies were mostly focused on the influence of Mg element on the precipitates evolution of the precipitation strengthening Cu–based alloys during heat treatment and its effect on the properties. However, as we known, Cu–Sn alloys are solid solution strengthening copper alloys [12], and the strengthening mechanism of Cu–Sn alloys is different from precipitation strengthening Cu–based alloys. To date, knowledge about the influence of the addition of Mg element on the microstructure evolution and properties of the Cu–Sn alloy is limited.
In present study, a Cu–0.29Sn–0.02Mg (wt.%) alloy was designed based on the commercial Cu–0.3Sn (wt. %) alloy, and the Mg-contained and Mg-free alloys were deformed by cold rolling. The microstructure and properties evolution of the Mg-contained and Mg-free alloys during the cold rolling deformation were investigated. The results of the research study could provide fundamental knowledge for optimal designing the Cu-Sn alloys with excellent comprehensive performance.

2. Materials and methods

Cu–Sn and Cu–Sn–Mg alloys were prepared in a vacuum induction furnace with the law materials of pure copper (99.99 wt.%), pure Sn (99.99%) and pure Mg (99.99%). At (1200 ± 10) °C, copper liquid was poured into the mold made of graphite die (20 mm × 80 mm × 120 mm). During the melting and casting process, high-purity argon was used to protect the melt from oxidation. The composition of the present Cu–Sn and Cu–Sn–Mg alloys measured by inductively coupled plasma emission spectroscopy (ICP, IRIS Intrepid II, thermo Fisher Scientific) is listed in table 1. After removing the casting defects on the ingots surface, the density of the Mg-contained and Mg-free samples were measured by material density meter (MDJ-600S, Xiamen xiongfa), and both the density of the Mg-contained and Mg-free samples is about ~8.90 g cm⁻³, suggesting that the addition of 0.02 wt.% Mg has little influence on the density of Cu–Sn alloy. The Mg-contained and Mg-free samples with the dimension of 18 mm × 20 mm × 100 mm were cut out and directly cold rolled by d250 mm double-roller mill with the reduction of 40%, 60%, and 80%, respectively.

Tensile testing samples were obtained from the as-cast and cold-rolled states specimens with a cross-section of 1 mm × 5 mm, and a gauge length of 25 mm. The tensile testing of the samples under different states were carried out on a CMT-5105 material testing machine at 293K, with a strain rate of 3 × 10⁻³ s⁻¹, to examine the mechanical strength of the Mg-contained and Mg-free alloys. Three samples were tested for each component to confirm reproducibility. EC values of the Mg-contained and Mg-free Cu–Sn alloys were tested by a direct current resistance tester at room temperature. Optical microscopy (OM) was employed to observe the microstructural of the Mg-contained and Mg-free Cu–Sn alloys under different states. Generally, the OM samples were first grinded and polished, and then corroded with 20% Greek HNO₃ aqueous solution. Transmission electron microscopy (TEM) observation of the deformed Mg-contained and Mg-free alloys were carried out on a FEI TecnaiG2–20 transmission electron microscope operating at 200 kV, and The TEM observation samples were prepared including the following steps. The samples were firstly ground to a thickness of about 50 um with SiC paper of 600–2000 meshes, and then punched into a disc with a diameter of 3 mm. Finally, the samples were subjected to electrolytic double spraying at a temperature of 238K. The double spraying liquid was a mixture of HNO₃ and C₂H₂OH at a ratio of 3:7. Further, The x-ray diffraction (XRD) measurements were carried out using an x-ray diffractometer (Xpert Powder, PANalytical B.V.) with Cu Kα radiation at 40 kV and 40 mA to identify the phases present and to obtain the dislocation density. The XRD samples were sequentially grounded using 600 to 2000 mesh SiC paper and electro polished with a mixed aqueous solution of 70 ml H₂O + 30 ml H₃PO₄ to remove the effect of grinding stress on lattice parameters.

3. Results

Figure 1 illustrates variation of ultimate tensile strength (UTS) and EC with different cold rolling reduction for the Mg-contained and Mg-free alloys. From figure 1(a), it can be found that the UTS of the as-cast Mg-contained and Mg-free alloys were similarly, and the EC value of the as-cast Mg-contained alloy (84.2%IACS) was slightly smaller than that of the as-cast Mg-free alloy (84.8%IACS). It is suggested that the addition of 0.02 wt.% Mg has a little influence on the mechanical strength and the microstructure of the as-cast Cu–Sn alloy. With the increase of the cold rolling reduction, both the UTS of the Mg-contained and Mg-free alloys was gradually increased, and the increment of the UTS of the Mg-contained alloy is obviously larger than that of the Mg-free alloy, which suggested that the addition of Mg can effectively increase the work hardening capacity of the Cu–Sn alloy. After 80% reduction, the UTS of the Mg-contained alloy (427 MPa) was larger than that of the Mg-free alloy (399MPa), the increment of the UTS contributed by Mg addition was about 28 MPa. Meanwhile, it also can be

| Sample     | Sn  | Mg  | Cu  |
|------------|-----|-----|-----|
| Cu-Sn      | 0.3 | 0   | Bal.|
| Cu-Sn-Mg   | 0.29| 0.02| Bal.|

Table 1. Chemical compositions of Cu–Sn and Cu–Sn–Mg alloys (wt.%).
seen that both the EC of the Mg-contained and Mg-free alloys was gradually decreased with the increase of the deformation degree, and the decrement of the Mg-contained alloy is slightly larger than that of the Mg-free alloy. After 80% reduction, the decrement of the EC of the Mg-contained alloy (80.1% IACS) was about 1.5% IACS when compared with the Mg-free alloy (81.6% IACS).

Figure 2 shows XRD patterns of the as-cast Mg-contained and Mg-free alloys. The XRD results show that both the as-cast Mg-contained and Mg-free alloys only consist of primary α-Cu phase and no second phase was formed, since the solubility of Sn and Mg in Cu is around 0.5wt.% and 1.0wt.% at room temperature, respectively.

Figure 3 shows the OM images of the Mg-contained and Mg-free alloys after different cold rolling reduction. From figures 3(a) and (b), it reveals that both the as-cast Mg-contained and Mg-free alloys were composed of equiaxed grains with a similar average grain size of about 500 μm, and no second particles were found in the matrix, which is similar to the XRD patterns results as shown in figure 2. During the cold rolling processing, the microstructure evolution trend of the Mg-contained and Mg-free alloys was similarly, the grain structure could be mainly classified into three stages. Firstly, the coarse grains were mainly divided by some deformation twins after 40% reduction (figures 3(c) and (d)). Secondly, the coarse grains were refined by the combined effects of deformation twins and deformation bands with the rolling reduction increases to 60% (figures 3(e) and (f)). Finally, further increasing the rolling reduction to 80%, as shown in figure 3(g) and h, grain refinement was mainly controlled by the deformation bands. However, with the increase of the cold rolling reduction, there are some differences can be observed between the Mg-contained alloy and Mg-free alloy. Firstly, there are more deformation twins in the Mg-contained alloy than that in the Mg-free alloy after 40% reduction (figure 3(d)). Secondly, it shows that the number of deformation bands is larger in the Mg-contained alloy than that in the Mg-free alloy after 60% and 80% reduction (figures 3(f) and (h)), leading to a more uniform grain structure in the
Cu–Sn–Mg alloy after 80% reduction. It is suggested that the addition of Mg could accelerate the grain refinement in Cu–Sn alloys during deformation.

To further investigate the influence of the addition of Mg on the microstructure evolution of the Cu–Sn alloy after cold rolling deformation, the Mg-contained and Mg-free alloys subjected to rolling reduction of 80% were observed by bright field TEM, as shown in figure 4. It shows that a large amount of dislocations were observed in both alloys, and many sub-structures [13] were also detected (figure 4). However, it can be obviously observed that significantly larger number density and more uniformly distributed sub-structures with an average size of 120 nm were formed in the Mg-contained alloy than that in the Mg-free alloy, indicating that the addition of Mg could enhance the sub-structures formation in Cu–Sn alloy during cold rolling deformation. Meanwhile, the dislocation density of the Mg-contained and Mg-free alloys after 80% reduction was also analyzed by XRD. The measurement results showed that the dislocation density in Mg-contained alloy ($1.39 \times 10^{13} \text{m}^{-2}$) is obviously larger than that of the Mg-free alloy ($0.59 \times 10^{13} \text{m}^{-2}$).
4. Discussion

The sub-structures formation was promoted by the addition of Mg. This can be explained from two aspects: Firstly, the diameter of the Mg atom (0.16 nm) is larger than that of the Cu atom (0.128 nm), which could lead to strong lattice distortion when Mg atoms dissolved into the Cu matrix, and contributed to the formation of more dislocation during deformation processing. Secondly, the dissolved Mg atoms are effectively in fixing the dislocations during deformation processing, resulting in higher number density of dislocations, and thereby accelerating the sub-structures formation [14].

As for solid solution strengthening copper alloys, the mainly strengthening mechanisms of the Cu–Sn alloys were solid solution strengthening, dislocation strengthening and grain boundary strengthening [15]. In the present study, because of the Mg addition amount is about 0.02wt.%, therefore it is suggested that the contribution of the solid solution strengthening by Mg atoms is neglect. As shown in figure 4(b), numerous fine sub-structures and high density of dislocation were formed in the Mg-contained alloy, since the sub-structure boundaries could effectively hinder the dislocations motion, resulting in a remarkable improvement in strength [16]. Therefore, it can be concluded that the increment of UTS of the Mg-contained alloy was mainly attributed to the grain boundary strengthening and dislocation strengthening.

However, the Mg atoms could cause lattice distortion and increase the electron scattering, leading to decrease the EC [11]. Therefore, a higher strength but lower EC was obtained in the Mg-contained alloy than that in the Mg-free alloy.

5. Conclusions

(1) The addition of Mg accelerated the grain refinement of Cu–Sn alloy. After cold rolling of 80%, the coarse grains were divided into small scale ones by deformation bands in Cu–Sn–Mg alloy.

(2) The addition of Mg promoted the sub-structure formation in the Cu–Sn alloy. Larger number density and more uniformly distributed sub-structures with an average size of 120 nm were formed in the Mg-contained alloy than that in the Mg-free alloy after cold rolling reduction of 80%.

(3) The addition of Mg improved the work hardening capacity, and improved the mechanical strength of the Cu–Sn alloy, but slightly reduced its EC. The UTS of the Mg-contained alloy after cold rolling reduction of 80% was improved by 28 MPa when compared with the Mg-free alloy, while its EC was slightly decreased by 1.5%IACS.

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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).

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