Effect of Cooling Methods on Microstructure and Mechanical Properties of Hot-extruded Cu-15Ni-8Sn Alloy

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Abstract: The effect of cooling method on microstructures and mechanical properties of the hot-extruded Cu-15Ni-8Sn bars were investigated by optical microscope(OM), scanning electronic microscope(SEM), differential scanning calorimetry(DSC) and tensile testing. The results indicated that the content of solid solution atom Sn in the water-cooled alloy after hot extrusion is greater than that in the air-cooled alloy. The precipitation onset temperature and dissolution termination temperature of γ phase in the water-cooled alloy are 24 °C and 32 °C lower than that in the air-cooled alloy, respectively. Both water-cooled and air-cooled alloys are composed of γ phase and supersaturated solid solution α(Cu), and show the similar grain size about 23 μm. In the air-cooled alloy, a large number of dispersed rod-like and granular γ-phases are precipitated in the grains, while only granular γ phase is observed in water-cooled alloy with . The tensile strength, elongation and microhardness of the water-cooled and air-cooled alloys are 588±12 MPa and 855±41 MPa, 41.6±2.0% and 15.2 ±1.0%, 166±7 HV and 292±5 HV, respectively, while the former shows a typical ductile fracture mechanism and the latter has somewhat brittle fracture characteristics.

1. Introduction

Cu-15Ni-8Sn alloys are considered as the most potential substitute materials for beryllium bronze, because it has high mechanical and physical properties equivalent to that of beryllium bronze, and has other valuable properties, such as excellent corrosion resistance, weldability, low cost, non-toxicity. Cu-15Ni-8Sn alloys show broad application prospects in the fields of electrical switches, chemical and marine components, and elastic sensitive components of precision instruments. In view of their excellent performance, they have been gradually applied to low-speed and heavy-duty bearings and heavy-duty bearings [1][2].

Cu-15Ni-8Sn alloys are a typical aging strengthening alloy, whose strength can be improved by proper thermomechanical treatments. According to some reports, the alloy can be achieved an ultrahigh strength (more than 1100 MPa) through cold deformation, but the loss of the plasticity is inevitably which is usually less than 3%. However, when the plasticity of the alloy exceeds 20%, its strength is sharply decreased to 655 MPa [3]. The increase in the strength of the alloy is mainly due to the amplitude modulation decomposition and order transformation during the aging process of the alloy, which will sacrifice the plasticity. At the same time, the discontinuous precipitation formed in the later stage of aging will reduce the mechanical properties of the alloy [1]. With the rapid development of modern industry, the requirements for the strength-ductility synergy of Cu-15Ni-8Sn alloy with large-sized bars are increasing. The traditional cold working preparation process (forging-cold drawing-solution aging) is difficult to achieve high strength and good ductility. While hot
extrusion process can effectively eliminate casting defects, and promote dynamic recrystallization to realize the grain refinement and thereby improve the strength and plasticity of the alloy [4]. The cooling methods after hot extrusion process show an important role in the saturation of the matrix and the characteristics of second phase (such as amount, distribution, morphology) which affect the spinodal decomposition and ordering transformation and further control the mechanical properties of the alloy.

Therefore, it is of great significance to study the influence of hot extrusion cooling methods on the microstructures and mechanical properties of the Cu-15Ni-8Sn alloy. However, few reports focus on this topic. In this paper, the effect of air and water cooling methods on the microstructures (especially the characteristics of γ phase) of hot-extruded Cu-15Ni-8Sn alloy is studied. Furthermore, the difference between mechanical properties of the alloys with air and water cooling is discussed.

2. Experimental materials and methods
The design composition of the experimental materials and the actual composition tested by the spectrum analysis are shown in Table 1. The as-received water-cooled and air-cooled bars are 100 mm in diameter. All experimental samples were taken from the periphery of the extruded bars. The samples for microstructural observation were etched in a solution containing 5 g FeCl3+10 ml HCl+100 ml H2O. The metallographic structure was observed with a German Leica DMI5000M metallurgical microscope and FEINONASEM430 and Quanta200 scanning electron microscope. Twenty effective fields of views were randomly selected for each sample, and the average grain size is measured by the cut-line method. The tensile test was carried out on the CMT5105 microcomputer-controlled electronic universal testing machine with a tensile rate of 0.5 mm/min. The tensile test specimens were prepared according to GB/T228-2002. The DSC samples were cut into a cylindrical sample with a diameter of about 3 mm and a height of 2 mm by wire cutting, and then ground to remove the oxide surface. The NETZSCH STA449C thermal analyzer was used with the experimental heating rate of 10 ℃/min, and the heating temperature range from 200 ℃ to 1280 ℃. The microhardness values (HV) were measured using an HVS-1000 microhardness tester with a load of 100 g and a dwell time of 10 s. Each test parameter sample at least 10 points were randomly selected for measurement under each condition.

| Design composition | Measured composition |
|--------------------|----------------------|
| Cu-15Ni-8Sn        | Cu 76.01 Ni 16.08 Sn 7.31 Fe 0.14 Mn 0.11 Zn 0.22 |

3. Experimental results and discussion
3.1. The effect of cooling methods on the microstructures
In order to a deep understanding of the difference between the precipitation behaviour of the second phase in the hot extruded alloy with the water-cooling (WC alloy) and the air-cooling (AC alloy), both WC and AC alloys were analysed through differential thermal scanning. The DSC curves of the alloys are shown in Figure 1, indicating that the temperature of the first endothermic peak is about 500℃. According to the literature [3], this peak is the precipitation peak of γ phase (Sn-rich phase), and the area of the precipitation peak is proportional to the amount of precipitated phases in the alloy [5]. The area of the precipitation peak is statistically found that the peak area in WC alloy is 4.1613 mWꞏ℃/mg, which is higher than that in AC alloy (2.3898 mWꞏ℃/mg). This increment in peak area indicates that the content of solid solution atom Sn in WC alloy is greater than that in AC alloy. The main reason is that the water cooling rate (about 150 ℃/s [6]) is faster than the air cooling condition (about 1 ℃/s [6])). Due to the rapid solidification associated with the water cooling process, Sn atoms are entrapped into the α-Cu lattice because of the lack of time present for precipitation of γ phase, leading to the formation of supersaturated solid solution in WC alloy. The values of the onset temperature, endothermic peak temperature and termination temperature of the precipitation peaks from Figure 1
were calculated and listed Table 2. The onset, peak and termination temperature values of the first endothermic peak of WC alloy are about 434 ℃, 547 ℃ and 596 ℃, respectively; while these values in AC alloy are about 458 ℃, 551 ℃ and 602 ℃, respectively. It is found that the onset temperature of the precipitation peak of the γ phase in the WC alloy is 24 ℃ lower than that of the air-cooled state alloy due to a relatively large chemical driving force for the precipitation of the γ phase resulted from the greater solution saturation in α-Cu matrix obtained by water cooling process. According to Zhao’s research [7], the second endothermic peak is the dissolution peak of the γ phase. The termination temperature of WC alloy is 808 ℃, which is 32 ℃ lower than that in AC alloy.

Figure 2 shows the microstructural features of the Cu-15Ni-8Sn alloys with air and water cooling. The grains of both AC and WC alloys show the fine and uniform grain structure with an average grain size about 23 μm (Fig. 2 (a-b)). Figure 2 (c) and (d) depict the longitudinal section (parallel to the extrusion direction) microstructure of the WC and AC alloys, showing that the grains are nearly equiaxed with no obvious fibrous structure. This phenomenon indicates that the dynamic recrystallization (DRX) was basically completed in AC and WC alloys [8].

The SEM images with a higher magnification (Fig. 3) shows the morphology of second phase, which is generally formed in the shape of rod-like and granular in AC alloy and only granular in WC alloy. Comparing with the WC alloy, AC alloys have a greater number of second phase with a more dispersed distribution. In order to investigate the composition and distribution of the second phase precipitated in these two alloys, the energy dispersive spectrum (EDS) analysis was employed and the results are shown in Table 3. The EDS results indicateshow that the alloys are consist of the α(Cu) matrix and Sn-rich γ phase , which is consistent with the literature results [4]. The content of Sn in the α(Cu) matrix of WC alloy is more than that in the AC alloy, which further indicates that the WC alloy shows a higher content of solid solution atom Sn. Based on the EDS mapping results, the trace elements Zn, Fe, and Mn are basically dissolved in the matrix of both alloys (Fig. 3(c-d)). According to J.C. Zhao’s research [7], the grain boundary and intragranular γ (DO3) precipitates would be formed above 593 ℃. Due to a relatively slower cooling rate of air cooling process, the AC alloy would stay a longer time above 593 ℃ during the cooling process, promoting the formation and growth of γ phase.

**Table 2** The values of onset peak and end temperature of first endothermic peak in WC and AC alloys

| Alloys  | Onset Temperatures (℃) | Peak Temperatures (℃) | End Temperatures (℃) |
|---------|------------------------|-----------------------|----------------------|
|         | Peak 1                 | Peak 1                | Peak 1               |
| WC alloy| 434                    | 547                   | 596                  |
| AC alloy| 458                    | 551                   | 602                  |
Figure 2 OM images of hot extruded Cu-15Ni-8Sn alloys with different cooling methods: water-cooled state: (a) cross (a) and longitudinal (b) section and (c) section; air-cooled state: (b) cross section, (d) longitudinal section

Figure 3 SEM images of the cross-section of the WC (a) and AC (b) Cu-15Ni-8Sn alloys; the high-magnification morphology and EDS mapping results of WC (c) and AC (d) alloys
### Table 3 Energy spectrum results (wt%) of corresponding positions in Figure 3

| Position | Cu     | Ni     | Sn     |
|----------|--------|--------|--------|
| 1        | 72.45  | 17.67  | 9.88   |
| 2        | 31.45  | 34.02  | 34.53  |
| 3        | 76.89  | 16.07  | 7.04   |
| 4        | 44.30  | 33.09  | 22.61  |
| 5        | 34.02  | 36.76  | 29.22  |
| 6        | 82.97  | 1.96   | 0.35   |

#### 3.2. The effect of cooling methods on the mechanical properties

Figure 4 shows the mechanical properties of hot-extruded Cu-15Ni-8Sn with air and water cooling processes. The tensile strength, elongation and microhardness of the WC alloy are 588±12 MPa, 41.6±2.0% and 166±7 HV, respectively, while these properties of the AC alloy are 855±41 MPa, 15.2±1.0% and 292±5 HV, respectively. It can be seen that the tensile strength and microhardness of AC alloy are 45.4% and 75.9% higher than those of the WC alloy, but the elongation of the AC alloy is significantly lower than that of the WC alloy. The increments in the strength and hardness are contributed to the large number of dispersed γ particles in the AC alloy, which improve the effect of precipitation strengthening resulted from hindering the movement of dislocations. However, the γ phase distributed at grain boundaries in the AC alloy would have a splitting effect on the matrix and thus deteriorate the ductility of the alloy.

![Figure 4](image1)

**Figure 4** Mechanical properties of AC and WC alloys: (a) the representative tensile curves; (b) the comparison of mechanical properties

![Figure 5](image2)

**Figure 5** Tensile fracture morphology of the WC (a) and AC (b) Cu-15Ni-8Sn alloys

The representative fractography images of the WC and AC Cu-15Ni-8Sn alloys are shown in Figure 5. The WC alloy shows the typical ductile fracture due to the formation of small dimples (Fig. 5 (a)), while some microcracks and a large number of shallow and small dimples were observed in the AC alloy. The fracture surface of the AC alloy is flat and bright, and no obvious “necking” phenomenon was observed, indicating that the AC alloy has a part of brittle fracture characteristics.
4. Conclusions

(1) The content of solution Sn in the matrix of the WC alloy is greater than that of the AC alloy. The precipitation onset temperature and dissolution termination temperature of the γ phase in the WC alloy are 24 ℃ and 32 ℃ lower than that of the AC alloy.

(2) The AC and WC alloys have similar microstructural features, which are consist of γ phase and supersaturated solid solution α(Cu) matrix with the average grain size about 23 μm. Compared with the amount and morphology of γ phase in WC alloy, a larger number of dispersed rod-like and granular γ particles are precipitated in the AC alloy, indicating that the formation and growth of γ phase are promoted during air cooling process owing to its relatively lower cooling rate.

(3) The tensile strength, elongation and microhardness of the WC and AC alloys are 588±12 MPa and 855±41 MPa, 41.6±2.0% and 15.2±1.0%, 166±7 HV and 292±5 HV, respectively. The dispersed γ particles in the AC alloy have an important role in the strength increment, while the deterioration of ductility of the alloy is attributed to the intergranular γ particles.

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