ORIGINAL RESEARCH

Columnar grains-covered small grains Cu–Sn alloy prepared by two-phase zone continuous casting

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Abstract A new theory of two-phase zone continuous casting (TZCC) has been established in order to improve mechanical properties, corrosion resistance and conductivity properties of metals with wide solid–liquid two-phase zone. A Cu–Sn alloy with continuous columnar grains-covered non-columnar small grains of same phase microstructure containing many self-closed grain boundaries were produced by the self-developed TZCC process. Compared with water-cooled mold continuous casting Cu–Sn alloy, the tensile strength and ductility of the TZCC alloy are greatly improved, the corrosion resistance is improved up to fifteenfold, and the conductivity is improved by 12.2%. The excellent high strength may be due to the effective blockage of dislocation motion by numerous self-closed grain boundaries, which suppress the propagation of grain boundary corrosion, and the extremely low electrical resistivity and high ductility may be attributed to continuous columnar grains.

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1. Introduction

The main problem for polycrystalline metals is that strength conflicts with ductility, i.e. strengthening is accompanied by a loss of ductility [1–3]. The corrosion resistance and conductivity of polycrystalline metals also seriously decline with improved strength [3,4]. All these issues are urgent and important since they restrict the application of polycrystalline metals. Hence, polycrystalline metals with high strength, ductility, corrosion resistance and conductivity are still pursued [3].

The properties of polycrystalline metals are influenced by their microstructures which consist of grains and grain boundaries [3–5]. These microstructures play a crucial role in strength, ductility, corrosion resistance and conductivity of metals [4–8]. Consequently, many processes have been developed to fabricate polycrystalline metals with different types of grains and grain boundaries based on solidification. For instance, equiaxed grains are obtained by using permanent mold casting, sand mold
casting, or conventional water-cooled mold continuous casting (WMCC) [9]. On the other hand, spherical grains are obtained by semi-solid casting [10], while continuous columnar grains are acquired by heated mold continuous casting (Ohno continuous casting, OCC) [11]. However, all the grains in conventional polycrystalline metals are mutually independent, and the grain boundaries of metals are interconnected [5]. As a result, metals are generally strengthened, but the ductility, corrosion resistance, and conductivity are remarkably decreased [3,5,12–14]. For example, metals with equiaxed grains have high strength due to their fine-grained microstructure with many grain boundaries [13–17], but their ductility and conductivity are relatively inferior; and also have poor corrosion resistance due to intergranular corrosion of abundant interconnected grain boundaries [5,18,19]. Recent studies showed that grain boundary engineering can improve strength, ductility and corrosion resistance of polycrystalline metals with equiaxed grains [20,21]. However, thermo-mechanical processing, which generates new special coincidence site lattice grain boundaries to destroy the connectivity of an original grain boundary network, is complicated, and the properties improvement is very limit. Other studies have demonstrated that increasing special grain boundaries and the discontinuity of a random grain boundary network in polycrystalline metals can decrease corrosion [22,23]. Conductivity also has a close relationship with grain boundaries [24], and a small number of grain boundaries lead to a high conductivity.

According to previous studies of continuous casting, continuous columnar grains can be formed when the temperature of the mold is above the liquidus (heated mold) [11], and small grains can be formed when the temperature of the mold is below the solidus (cold mold) [25]. However, a solid–liquid two-phase zone between the liquidus and solidus also exists in many metals. In the two-phase zone, both liquid phase and small grains of solid phase can exist. If the liquid phase is controlled to form continuous columnar grains and the small grains of solid phase are retained during continuous casting at the temperature of the mold in the two-phase zone, a new continuous casting process can accordingly be developed, here called as two-phase zone continuous casting (TZCC).

In this paper, we try to control the temperature of the mold between the liquidus and solidus of metal during continuous casting, and experimentally investigate the Cu–Sn alloy with wide solid–liquid two-phase zone prepared by TZCC process. The microstructure of TZCC Cu–Sn alloy is analyzed. The mechanical properties, corrosion resistance and conductivity properties of the TZCC Cu–Sn alloy plates are investigated, and compared with WMCC Cu–Sn alloy. Influence mechanism of microstructure on properties of the TZCC Cu–Sn alloy is discussed.

2. Experimental

Fig. 1 shows the schematic diagrams of TZCC. The metal is heated in the graphite crucible by the induction heating coil to melt and keep liquid phase, which shows in Fig. 1 as “liquid zone”. Liquid metal flows into graphite mold which connects with the bottom of graphite crucible. In addition, the temperature of the graphite mold is controlled at the two-phase zone by the temperature-controlling induction coil, and the exit of the mold where the metal has been solidified is forced to cool (Fig. 1 shows as “cooling water”).

In the present study, a Cu–4.7 wt%Sn alloy with wide two-phase zone was used as the raw material. The alloy was prepared by induction melting under an Ar atmosphere in a graphite crucible at the temperature of 1200 °C. Meanwhile, the temperature of the mold was controlled between the liquidus and solidus according to the Cu–Sn phase diagram by the temperature controlling induction coil system. This system had two temperature controlling points which were set at the entrance (1040 °C) and exit (920 °C) of the mold in order to detect the temperature of the mold. The alloy was kept for 20 min at the setting temperature of the crucible for homogenizing prior to continuous casting. With the liquid Cu–Sn alloy continuously feeding into the graphite mold, the alloy was solidified under 18 °C and 400 L/h of intensive water cooling, and then it was pulled out of the mold by traction wheels with dummy bar of pure copper. The Cu–Sn alloy plates with a width of 20 mm and a thickness of 5 mm were continuously fabricated at a constant speed of 20 mm/min. Cu–Sn plates with the same composition of Cu–4.7 wt%Sn were also fabricated by conventional WMCC equipments.

Three TZCC Cu–Sn alloy samples were chosen to anneal under an Ar atmosphere with the annealing time of 300 min and the annealing temperatures of 650, 750 and 850 °C, respectively. The microstructures of same position in as-cast and annealed samples were observed.

The mechanical properties were carried out by tensile testing machine, and corrosion resistances were tested at the temperature of 20, 50, and 80 °C. Conductivities of TZCC and WMCC Cu–Sn alloy were also tested by four-point collinear probe method.

The scanning electron microscope (SEM) image was characterized on a LEO-1450, which was equipped with the energy dispersive spectrometry (EDS), and the Euler angles orientation map was measured by an Oxford Instruments-HKL Channel 5 Electron Back-Scattered Diffraction (EBSD) system. The optical microstructure (OM) was performed by using Nikon Coolpix 995 optical microscope. The Vickers hardness pyramid indenter was used to test hardness of the covered small grains and continuous columnar grains in the TZCC Cu–Sn alloy. EDS was used to analyze the chemical composition. An X-ray diffractometer was used to analyze the phase of the sample.

3. Results and discussion

3.1. Microstructures and analysis of columnar grains-covered small grains Cu–Sn alloy

Fig. 2a is SEM images of the microstructure of the TZCC Cu–Sn alloy, in which continuous columnar grains and small grains obtained by the OCC and WMCC process respectively are contained, and numerous small grains (indicated by red arrows) are covered by continuous columnar grains (indicated by blue arrows). It can be found that the microstructure of the TZCC Cu–Sn alloy is completely different from the existing microstructure of alloys. Such a new continuous columnar grains-covered small grains (columnar grains, CCGs) microstructure that has never been reported is proven to exist in the previous conventional alloys. The Euler angles orientation map (Fig. 2b) was obtained by EBSD, and the different
Euler angles of the continuous columnar grains and small grains are represented by the different colors. We can see that grain A (in Fig. 2b), an independent existence with self-closed grain boundary, has distinct color from surrounding and vicinity grains. In other words, grain A has no any relationship with surrounding and vicinal grains. Similarly, grain B (in Fig. 2b) means a small grain between continuous columnar grains. The optical microstructures of the alloys (Fig. 2c, d) show many self-closed grain boundaries (indicated by black arrows) exist instead of the interconnected grain boundaries (indicated by yellow arrows). The black dots (in Fig. 2d) scattered in the microstructures are dispersed shrinkage. In addition, numerous small grains without interconnected grain boundaries and large orientational grains similar to the continuous columnar grains microstructure are obtained. To further reveal the GCGs microstructure, a plate sample was cut into two sides for optical observations (Fig. 2e). From the microstructure of each side, some small grains are covered by a continuous columnar grain in the right side, but none in the left side. Subsequently, to scrutinize the microstructure, the right side of the sample was gradually ground until the covered small grains were all worn away. The same continuous columnar grain that covered the above small grains is still visible, confirming that the small grains are entirely covered by the continuous columnar grain. The metallographs of the TZCC Cu–Sn alloy confirm that during growing from the exit of the mold to the liquid phase, the continuous columnar grain encloses the small grains that form at the inner sidewall of the mold and then fall into the front of the solidification interface, as shown in Fig. 1.

In situ optical observation of as-cast and annealed alloy was carried out. After annealing at 650 °C for 300 min, the morphology of small grain in the sample (Fig. 4b) is the same as that in its as-cast sample (Fig. 4a). Fig. 4c shows that there are four neighboring small grains, which are marked by A, B, C and D. After annealing at 750 °C for 300 min, only one grain (marked by E) remains, as shown in Fig. 4d. It implies that grain boundary migration of small grain occurs during annealing, while some grains disappear. Some small grains with self-closed grain boundary in the as-cast sample starts to disappear after annealing at 850 °C for 300 min, i.e., the small grain in the as-cast sample (Fig. 4e) cannot be found at the same position in the annealed sample (Fig. 4f).
Increasing temperature and time of annealing is conducive to vacancy diffusion of grain boundary, which causes grain boundary migration. Therefore, grain boundary migration occurs at high temperature for an adequate time. The direction of grain boundary migration is towards the center of curvature of the grain boundary. As a result, some small grains disappear.

3.2. Mechanical properties and mechanism of the columnar grains-covered small grains Cu–Sn alloy

Tensile tests were carried out to evaluate strength and ductility of the continuous casting Cu–Sn alloy, and the engineering stress–engineering strain curves are shown in Fig. 5a. The tensile strength of the TZCC Cu–Sn alloy reaches 255 MPa, and the elongation to failure reaches 49%. By comparison, the WMCC Cu–Sn alloy with equiaxed grains was also tested, and its tensile strength is 220 MPa with an elongation to failure of 35%. This new type of GCGs microstructure exhibits a much higher plasticity as well as strength.

When the tensile deformation of the TZCC Cu–Sn alloy proceeds, more and more dislocations pile up inside the self-closed grain boundaries, which obstruct the deformation of the covered small grains. Due to no transverse grain boundaries leading to dislocation pile up during the tensile deformation, the continuous columnar grains have high ductility and can deform to a great extent. It means that the TZCC Cu–Sn
alloy can deform to a great extent and exhibit a high ductility, although the deformation of the covered small grains become more difficult during tensile deformation. For the WMCC Cu–Sn alloy, however, numerous dislocations pile up at the grain boundaries of the equiaxed grains at the early stage of tensile deformation. When the deformation of the WMCC Cu–Sn alloy proceeds, a high density of dislocations tend to pile up at grain boundaries and induce high stress concentration. When the local stress is high enough and cannot be effectively released by dislocation slip, microcracks form and induce the premature fracture. Hence, the WMCC Cu–Sn alloy has a low elongation.

The increase in the tensile strength of the TZCC Cu–Sn alloy is mainly attributed to the self-closed grain boundaries of the covered small grains. Dislocations tend to concentrate inside the self-closed grain boundaries of the covered small grains during the deformation of the covered small grains. Meanwhile, with the deformation of the continuous columnar grains, dislocations gradually pile up outside the self-closed grain boundaries. Consequently, large quantities of piled-up dislocation “islands” exist in the region where the covered small grains scatter in the continuous columnar grains. Dislocations also concentrate in the grain boundaries of the continuous columnar grains during deformation. Such behaviors make the motion of dislocation more difficult, and both the deformation resistance and tensile strength of the TZCC Cu–Sn alloy increased as well.

### 3.3. Corrosion properties and mechanism of the columnar grains-covered small grains Cu–Sn alloy

Corrosion rate tests were carried out to evaluate the corrosion resistance of the continuous casting Cu–Sn alloy. The samples with dimension of 50 mm × 20 mm × 5 mm were separately cut along the longitudinal direction of TZCC and WMCC Cu–Sn alloys. The original alloy surface layer was removed by sandpaper to ensure uniformity of the results. Then, the samples were immersed in the corrosion solution (10% HCl) ensuring no contact with the container wall. The amount of test solution for the surface area of the samples was not less than 20 mL/cm². Water bath temperatures of 20, 50, and 80 °C were selected. The samples were taken out every 24 h, clearly rinsed, and then pickled in a 50% HCl solution under ultrasonic vibration for 3 min. The corrosion rate was calculated by the following equation:

\[
V = \frac{M - M_f}{ST}
\]

where \(V\) is the corrosion rate, \(M\) is the mass of the sample before corrosion, \(M_f\) is the mass of the sample after corrosion, \(S\) is the total surface area of the sample, and \(T\) is the time of the test.

The results in Fig. 5b show that the corrosion rates gradually increase with time. This trend can be explained by the fact that the alloy dissolved in the solution, and electrochemical corrosion gradually occurs with the increase of the time. The corrosion rate is greatly improved because increasing temperature increases the rate of the chemical reaction.

From the above corrosion results, it can be found that the TZCC Cu–Sn alloy has a much higher corrosion resistance than that of the WMCC one. For example, at the temperature of 80 °C and the test time of 120 h, the corrosion rate (31.99 g/m² h) of the WMCC Cu–Sn alloy is fourfold more than that (7.86 g/m² h) of the TZCC, and at the temperature of 20 °C and the test time of 168 h, the corrosion rate (16.14 g/m² h) of the WMCC Cu–Sn alloy is fifteenfold more than that (1.06 g/m² h) of the TZC. Since many small grains covered by continuous columnar grains have only self-closed grain boundaries, the propagation of grain boundary corrosion is suppressed.

### 3.4. Conductivity properties and mechanism of the columnar grains-covered small grains Cu–Sn alloy

Resistivity tests were conducted to evaluate the conductivity of the continuous casting Cu–Sn alloy. Samples with dimension of 2 mm × 2 mm × 30 mm were cut along the longitudinal
direction. A four-point collinear probe method was used to measure resistivity. Two probes were used for the current testing, and the other two were used for the voltage testing. The resistance of Cu–Sn alloy samples can be determined, and the resistivity of the alloy was calculated by the following equation:

\[ \rho = \frac{R \times A}{l} \]  \hspace{1cm} (2)

where \( \rho \) is the resistivity, \( R \) is the resistance, \( A \) is the cross-sectional area of the sample, and \( l \) is the length of the sample.

Conductivities are calculated by \( 1/\rho \). At room temperature, the resistivity of the TZCC Cu–Sn alloy is only \( 8.937 \times 10^{-6} \) \( \Omega \) cm, whereas that of the WMCC Cu–Sn alloy reaches \( 1.003 \times 10^{-5} \) \( \Omega \) cm. Fig. 5c shows the conductivity of the alloys. The conductivity of the TZCC Cu–Sn alloy is increased by 12.2% compared with the WMCC Cu–Sn alloy. This trend is ascribed to that the current transportation in the TZCC Cu–Sn alloy mainly passes through continuous columnar grains, and small grains in the columnar grains occupy small area and have a small action of electron scattering, as a result, the conductivity of the TZCC Cu–Sn alloy was obviously improved.

4. Conclusion

1) A new GCGs microstructure, which consists of grains-covered grains and self-closed grain boundaries, can be obtained in Cu–Sn alloy with wide solid–liquid two-phase zone by the novel TZCC (two-phase zone continuous casting) process.

2) The tensile strength of the TZCC Cu–Sn alloy reaches 255 MPa, and the elongation to failure reaches 49%. Compared with WMCC Cu–Sn alloy, the tensile strength and ductility of the TZCC alloy are greatly improved.

3) The corrosion rate of the TZCC Cu–Sn alloy is 1.06 g/m²·h at 20 °C and test time of 168 h. Compared with conventional water-cooled mold continuous casting
Cu–Sn alloy, the corrosion resistance of TZCC Cu–Sn alloy is improved up to fifteenfold. This may be attributed to the fact that in TZCC Cu–Sn alloy, the self-closed grain boundaries suppress propagation of grain boundary corrosion.

4) Compared with WMCC Cu–Sn alloy, the conductivity of TZCC Cu–Sn alloy is improved by 12.2% at room temperature.

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