Cu-10Sn-4Ni-3Pb Alloy Prepared by Crystallization Under Pressure: An Experimental Study

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The wear-resistant tin bronze (Cu-10Sn-4Ni-3Pb) with tin content above 8 wt.% prepared by traditional melting and casting process usually defects such as low density, poor properties and segregations. The crystallization under pressure processing of Cu-10Sn-4Ni-3Pb alloy was investigated. The microstructures were observed and analyzed and compared with that by traditional melting and casting process. The results show that the dendrite has obviously disappeared and the dendritic segregation alleviated by using the crystallization under 680 MPa pressure process, in comparison with the remarkably dendrite microstructure and severe as-cast defects of alloy prepared by traditional melting and casting technology. Based on the experimental study, the properties and microstructures of Cu-10Sn-4Ni-3Pb tin bronze prepared by crystallization under pressure have been improved significantly.

KEY WORDS: Cu-10Sn-4Ni-3Pb bronze; Crystallization under pressure; Microstructure; Segregation

1. Introduction

Tin bronzes containing lead and nickel are mainly used to produce the wear parts such as bearings, impellers, sleeves and gears due to good wear and corrosion resistance and excellent mechanical performance^[1]. The variations of tin composition will significantly affect alloy characteristics and properties^[2,3], for instance, with the increasing of tin content in industrial tin bronze alloy (3 wt.%–14 wt.% Sn), the wear resistance of tin bronze will be improved while its density and plasticity decreased. For the tin bronze with tin content more than 8 wt.%, the serious problems such as lower density, more as-cast defects and obvious segregation will be caused by using the traditional melting and casting process^[4]. Furthermore, due to the higher tin content, the plasticity of alloy is extremely inferior and its performance and

microstructure are difficult to improve through plastic forming process.

Halvae and Talebi^[5] investigated the effect of process variables including pouring temperature, mould rotation speed and mould cooling rate on the microstructure and segregation of tin bronze. You *et al.*^[6] presented the best process parameters of vacuum differential pressure casting tin bronze cover. The effects of Fe, Mn and P elements on the wear resistance of Cu-Sn-Zn-Pb bronzes have been experimentally investigated, as referred by Turhan^[7]. According to Park and Voyakin^[8], the adding elements such as Sn, Zn and Pb have been played the key role on microstructure and mechanical properties of tin bronze alloy. Lin *et al.*^[9] have provided an overview of the microstructure and mechanical properties of ZQSn10-2 tin bronze by adding a small amount of nickel and diffusion annealing treatment. Ünlü *et al.*^[10] outlined the effect of alloy elements such as copper, tin and zinc on tribological and mechanical properties of CuSn10 bronze bearings. There is no direct correlation between mechanical properties and wear response of leaded-tin bronzes, as demonstrated

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by Prasad^[11]. Most of above investigations focused on the melting and casting preparation process and performance of high-tin general tin bronze, partially on the plastic forming technology and properties of some tin bronze containing Sn less than 8 wt.%. However, according to the high-tin wear-resistant tin bronze alloy including Sn more than 8 wt.%, there are no reports about the advanced preparation technology which can improve the density and segregation simultaneously.

Therefore, the aim of this study is to investigate the new crystallization under pressure processing of Cu-10Sn-4Ni-3Pb alloy containing 8 wt.%–12 wt.% Sn. In comparison with the traditional melting and casting process, the tin bronze prepared by this new process has the refining grains and its dendritic segregation was eliminated. So the research is of greater guidance and reference significance to the preparation of tin bronze alloy with higher tin content.

2. Experimental

The crystallization under pressure process route preparing Cu-10Sn-4Ni-3Pb alloy includes proportioning, melting, insulation, pouring and extrusion. The concrete procedures are: (1) Proportioning. The raw materials of 99.95% Cu, 99.90% Sn, 99.99% Ni and 99.994% Pb were selected and their contents were 83 wt.%, 10.5 wt.%, 3.5 wt.%, 3.0 wt.%, respectively. (2) Melting. The melting process was carried out in the KGPT200-2.5 Medium Frequency Induction Furnace under partial-pressure oxidization atmosphere by feeding copper, then nickel, tin and lead. The raw materials were melted in a temperature range from 1150 °C to 1250 °C and the P-Cu deoxidizer was used to deoxidization. (3) Insulation. The molten was transformed into a holding furnace for heat preservation and the final slag skimming treatment was done. The holding temperature range was from 1150 °C to 1200 °C. (4) Pouring and Extrusion. The molten was

poured into preheated extrusion cavity die from holding furnace and then extruded rapidly under the Y32-500 oil press. The extrusion pressure was 680 MPa and the pressure holding time was two minutes. The green compact was 97 mm in diameter.

As a compared experiment, the traditional melting and casting process route for preparing Cu-10Sn-4Ni-3Pb alloy is proportioning, melting, pouring and solidification in graphite casting mold.

The actual compositions were tested by chemical analysis method. The density was measured by the Archimedes water immersion method. Hardness was measured on HB-3000 Brinell hardness tester. Samples were corroded by immersion into 30% HNO₃ solution for 10–15 min, and then wiped using industrial sodium carbonate before water cleaning. The radial section macrostructure of samples was observed directly with the naked eyes at room temperature. The microstructure of samples was observed and analyzed through optical microscope (OM; Model OLYMPUSPMG3), scanning electron microscope (SEM; Model JSM-5610LV) with energy dispersive X-ray spectrum (EDS), and transmission electron microscope (TEM; Model JEM-2100), respectively. The actual compositions of Cu-10Sn-4Ni-3Pb alloys prepared by traditional melting and casting process (No.1) and crystallization under 680 MPa pressure process (No.2), respectively, have been gathered in Table 1.

3. Results

Table 1 indicates that the Cu-10Sn-4Ni-3Pb alloy

Table 1 Actual compositions (wt.%) of Cu-10Sn-4Ni-3Pb samples prepared by different processes

No.	Sn	Ni	Pb	P	Cu
1	10.39	3.45	3.19	0.013	Bal.
2	10.23	3.44	3.12	0.015	Bal.

Fig. 1 Radial section macrostructures of Cu-10Sn-4Ni-3Pb samples prepared by different processes: (a) as-cast; (b) as-extruded

properties have been improved significantly by crystallization under pressure process (No.2). The density and hardness of as-extruded alloy using this new process are 9.04 g/cm^3 and 129 HB, in comparison with 8.94 g/cm^3 and 112 HB of as-cast alloy prepared by traditional process, they have been increased by 1.1% and 15.2%, respectively.

Fig. 1 shows the radial section macrostructure of Cu-10Sn-4Ni-3Pb samples prepared by different processes after corrosion treatment. As it can be seen in Fig. 1(a), the fine equiaxed grain shell has been formed only beside the casting inner wall, and then the interface grown with dendrite array and formed a large number of columnar crystal. The whole radial section macrostructure is consisted of dendrite structure. Fig. 1(b) shows that the grains have been obviously refined by crystallization under pressure process and the whole radial section macrostructure is mainly composed of fine equiaxed grains.

The microstructure of Cu-10Sn-4Ni-3Pb samples prepared by traditional melting and casting process is presented in Fig. 2. It has been found that the dendrite microstructure with some random orientation is obvious in as-cast Cu-10Sn-4Ni-3Pb alloys prepared by traditional process. The white crystal axis of dendrite center is mainly consist of substitution solid solution in which the tin dissolved into copper and the gaps of alpha dendrite are off-white ($\alpha+\delta$) eutectoid. The lead particles in the form of simple substance phase have been distributed among the Cu-matrix which can improve the wear resistance of Cu-10Sn-4Ni-3Pb alloy (Fig. 2(b)).

The as-cast microstructure and micro area composition of Cu-10Sn-4Ni-3Pb alloy was studied by using SEM equipped with EDS. Due to the different atomic numbers of copper, tin, nickel and lead element included in Cu-10Sn-4Ni-3Pb alloy, the alloy micro area composition can be analyzed qualitatively based on the contrast variation. Fig. 3(a) and Fig. 3(b) show that the higher atomic number areas such as lead on the sample present brighter images due to collecting more backscattered electrons, while the tin and copper areas are dark images. Therefore, the crystal axis of dendrite center is white and the black lead single particles in metallograph present white, which

can be observed obviously by EDS analysis in Fig. 3(c) and Fig. 3(d). The TEM micrographs of as-cast Cu-10Sn-4Ni-3Pb alloy prepared by traditional melting and casting process have been shown in Fig. 3(e) and Fig. 3(f). As it can be seen in Fig. 3(e), a large number of dislocations distribute among the Cu-10Sn-4Ni-3Pb alloy matrix, and then formed the dislocation pile-up phenomenon (Fig. 3(f)).

The microstructure of Cu-10Sn-4Ni-3Pb samples prepared by the crystallization under 680 MPa pressure process has been seen from Fig. 4. As it can be seen in Fig. 4, the most dendrites have been replaced by a large number of fine grains like as equiaxed crystals. The results of the microstructure and micro area composition of Cu-10Sn-4Ni-3Pb alloy prepared by crystallization under 680 MPa pressure using SEM equipped with EDS have been gathered in Fig. 5. In comparison with the as-cast microstructure, the dendrites disappeared obviously and the dendritic segregation alleviated in as-extruded microstructure. Though the basic microstructure normally includes a matrix of alpha phase, ($\alpha+\delta$) eutectoid and lead single phase, the number of ($\alpha+\delta$) eutectoid decreased remarkably, and the size and distribution of the lead particles on Cu-matrix changed significantly. Further, it has been confirmed from the Fig. 5(c) and Fig. 5(d) that most self-lubrication lead particles distribute around the grain and grain boundary, which can play an important role on improving the hardness and wear resistance for Cu-10Sn-4Ni-3Pb alloy. Fig. 5(e) shows that high density dislocations and particulate precipitates distribute in copper matrix with the entwinning structure. The grain boundary and twin interface with the coherent characteristic have been observed obviously and a large amount of granular precipitates with average grain sizes of about 10–20 nm distributed dispersively on both sides of twin interface (Fig. 5(f)).

4. Discussion

An analysis of equilibrium Cu-Sn phase diagram indicated that the solidification and crystallization process include a peritectic reaction ($L + \alpha \leftrightarrow \beta$) at 799°C and three eutectoid reactions, which are $\beta \leftrightarrow \alpha + \gamma$ at 586°C , $\gamma \leftrightarrow \alpha + \delta$ at

Fig. 2 Metallographs of as-cast Cu-10Sn-4Ni-3Pb samples prepared by traditional melting and casting process: (a) low magnification; (b) high magnification

Fig. 3 Microstructures and EDS analysis of as-cast Cu-10Sn-4Ni-3Pb samples prepared by traditional melting and casting process: (a, b) SEM images; (c, d) EDS analysis; (e, f) TEM images

Fig. 4 Metallographs of as-extruded Cu-10Sn-4Ni-3Pb samples prepared by crystallization under 680 MPa pressure: (a) low magnification; (b) high magnification

Fig. 5 Microstructures and EDS analysis of as-extruded Cu-10Sn-4Ni-3Pb samples prepared by crystallization under 680 MPa pressure: (a, b) SEM images; (c, d) EDS analysis; (e, f) TEM images

520 °C and $\delta \leftrightarrow \alpha + \eta$ at 350 °C, respectively^[12]. Due to the solidification under non-equilibrium conditions, the crystallization temperature range expanded and alpha phase become narrow in Cu-10Sn-4Ni-3Pb tin bronze alloy. The peritectic reaction ($L + \alpha \leftrightarrow \beta$) occurred and produced beta phase at 799 °C, and then two eutectoid reactions ($\beta \leftrightarrow \alpha + \gamma$, $\gamma \leftrightarrow \alpha + \delta$) also take place subsequently at higher temperatures of 586 °C and 520 °C. However, with the temperature decreasing ulteriorly, eutectoid reaction ($\delta \leftrightarrow \alpha + \eta$) has not happened at lower temperature of 350 °C, because tin atom radius is larger and its diffusion rate in copper is very slow, which resulted in hard and brittle δ -phase with complex body-centered cubic structure decomposing hardly. Thus, in the room temperature as-cast microstructure of Cu-10Sn-4Ni-3Pb alloy is consisted by alpha solid solution, ($\alpha + \delta$) eutectoid and lead single particles under practical condition.

Based on the classic metal solidification theory^[13], the negative temperature gradient has been built up in the liquid-solid interface front when the Cu-10Sn-4Ni-3Pb alloy molten was poured into graphite mould, and then the temperature gradually reduces and undercooling increases from crystalline solid surface to internal alloy liquid. When some solid phase protrudes into liquid phase region of liquid-solid interface frontier with larger undercooling, the L/S interface frontier will no longer remain the plain state and form more crystal axis like branches (dendrite). With the growing of crystal axis, the latent heat of fusion releases and accesses the supercooling liquid region through heat conduction, which lead to the temperature increasing from liquid to solid, and then the secondary, the third etc. dendrite arms perpendicular to the crystal axis formed in accordance with the order, and the remaining liquid could be solidified in

the form of flat growth way finally. Throughout the course of dendrite formation and growth, the under-cooling liquid phase absorbs the released latent heat and the dendrite grows according to a certain direction. In addition, the reasons leading to the quantity dendrite existence in the prepared alloy by traditional process are that the copper, tin, lead and nickel are included in the wear-resistant Cu-10Sn-4Ni-3Pb alloy. These four elements have different characteristics in physical properties, solidification feature and the interface relationship between element and copper matrix, which lead to different diffusion rates and solidification sequences during melting and crystallization processes of multiple element alloy. Copper has the higher melting point and nickel solidifies preferentially and forms white crystal axis of dendrite, on which α solid solution appeared, namely the substitution solid solution of tin forms on copper matrix^[14]. The off-white eutectoid ($\alpha+\delta$) distribute among the gaps of dendrite skeletons, in which the hard phase δ can improve the hardness and wear-resistance. Lead element having low melting point and hardly dissolved in copper distributes around the grain and grain boundary in the form of black particle simple substance phase, which has the self-lubricating function and can reduce friction coefficient and improve density and wear-resistance of the alloy^[15]. However, the nickel element can be entirely dissolved in copper matrix, which promoting the dendrite growth and refining grains. In addition, it also can alleviate the lead segregation and improve the strength and thermal stability of the alloy. When the molten was poured into the graphite casting mold, the growth of equiaxed grains are limited as the slower cooling rate in casting process, which lead to growing adequately of α phase and forming restrictedly of eutectoid ($\alpha+\delta$). Therefore, the as-cast microstructure of Cu-10Sn-4Ni-3Pb samples prepared by traditional melting and casting process are mainly thinner and longer dendrites with a certain orientations (Fig. 2). Furthermore, due to the producing of defects such as hot cracks, segregation, shrinkage cavity and porosity by gravity pouring under atmosphere easily, it can be interpreted that Cu-10Sn-4Ni-3Pb alloy prepared by traditional melting and casting process has lower properties such as density and hardness.

Unlike obvious dendrite in as-cast microstructure, the crystallization under pressure process investigated in this paper suggests that the poured molten should be extruded directly under instantaneous larger pressure when it still remain the liquid or semi-solid states, and the crystallization process of alloy molten happened nearly simultaneously. The dendrites have not enough time to nucleate and grow, and even the formed dendrite skeletons also have been broken and melted under the after pressure. So the macro and micro segregation of the dendrites have been eliminated, the whole alloy sections are mainly with the fine equiaxed crystals (Fig. 4). Furthermore, the de-

formation resistance of the alloy reduced due to the effect of pressure, and the as-cast defects were eliminated effectively. Therefore, the properties such as density and hardness of Cu-10Sn-4Ni-3Pb alloy prepared by crystallization under pressure were improved significantly.

On the basis of atomic scale analysis, the plastic deformation of Cu-10Sn-4Ni-3Pb alloy with entirely liquid or semi-solid state was realized under extrusion pressure. The crystal vacancy at high temperature equilibrium concentration accumulated along crystal face and formed vacancy clusters under the larger extrusion pressure^[16]. The dislocation loops were produced when the vacancy clusters developed to a certain extent and took place collapse, which lead to the appearance of abundant dislocations in the internal of material^[17]. In addition, the distribution of netlike serried dislocations within the crystal is uneven, in which the high density entwining dislocations mainly concentrate around the dislocation cells and lower dislocation density in the intracellular (Fig. 5(e)). On the other hand, owing to the high energy state after deformation of the whole system of alloy, the defects such as vacancy and dislocation within the crystal were easy to move, which provides an advantage for the nucleation and growth of precipitates. The alloy element precipitations along crystal boundary were prevented and their distribution was more dispersed consequently, which formed a large number of pinning points in the copper matrix. Meanwhile, due to the smaller precipitated phase particles and particle spacing, the dislocation aggregates and proliferates constantly during the process of moving and results in the higher dislocation density finally. According to the Orowan stress mechanism^[18], the moving resistance of dislocation lines has been increased and slip resistance enhanced under the interactions of precipitations and dislocations, which produced strong work hardening effect on improving alloy strength. Meanwhile, the twin boundary was observed on the Cu-matrix and the crystal plane atoms retain a coherent lattice relationship with matrix (Fig. 5(f)). Owing to the twin boundary hindering effect to slip and the existence of lattice distortion on grain boundary, the comprehensive mechanical properties of Cu-10Sn-4Ni-3Pb alloy prepared by crystallization process under 680 MPa have been improved significantly.

5. Conclusions

The Cu-10Sn-4Ni-3Pb alloy properties such as density and hardness have been improved significantly by crystallization under pressure process. The grains have been obviously refined and the whole radial section macrostructure is mainly composed of fine equiaxed grains. In comparison with the remarkable dendrite microstructure and the severe dendritic segregation of as-cast alloy, which is mainly consist of α solid solution, ($\alpha+\delta$) eutectoid and lead simple

substance phase, the most dendrites disappeared and the dendritic segregation alleviated in as-extruded microstructure. The number of ($\alpha+\delta$) eutectoid decreased remarkably, the size and distribution of lead particles on Cu-matrix changed significantly. In addition, a large amount of granular precipitates in average grain sizes ranging from 10 nm to 20 nm distributed dispersively on both sides of twin interface. Through the comprehensive comparison of process route, properties and microstructures, the crystallization under 680 MPa extrusion pressure is superior to the traditional melting and casting process.

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