

Research Article

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Solidification microstructure characteristics of Cu–Pb alloy by ECP treatment

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Abstract: The effects of high-density electric current pulse (ECP) treatment on the solidification of Cu–37.4 wt% Pb monotectic alloy melt were investigated. Compared to the method of molten glass purification combined with cyclic superheating, ECP treatment created finer microstructures of Cu–Pb alloys, with more homogeneous distribution of the Pb phase in the matrix. This phenomenon can be explained by the cluster theory for liquid metals and the non-equilibrium diffusion theory. First, ECP treatment could cause the fission of larger atomic clusters to increase the undercooling that enabled a large number of smaller clusters to grow and reach the critical nucleation radius. Second, ECP treatment could reduce the diffusion energy barrier to enhance the non-equilibrium diffusion of solute atoms and suppress the segregation of Pb.

Keywords: electric current pulse, undercooling, grain refinement, solidification structure, Cu–37.4 wt% Pb alloy

1 Introduction

Cu–Pb immiscible alloys have been of great interest due to their wear resistance and superconducting properties, and they are considered as advanced bearing materials when the soft Pb phase is homogeneously dispersed in a hard Cu matrix. However, the Cu–Pb phase diagram is often characterized by miscibility gaps in the liquid state [1,2]. When the homogeneous liquid metal is cooled into

miscibility gaps, the components become immiscible and lead to the separation of two liquid phases. The mechanical properties of alloys highly depend on phase separation and microstructural evolution. The lack of homogeneous microstructure could reduce the anti-friction performance and fatigue strength of alloys [3,4]. To overcome the immiscibility of different phases in alloys, many efforts have been made to regulate liquid phase separation in alloys, such as rapid solidification of highly undercooled melts and the addition of a third component [5,6].

The electric current pulse (ECP) treatment has great potential to control the formation of solidification microstructures in metallic alloys. The ECP treatment can increase the heterogeneous nucleation rate of liquid (and semi-liquid) metals, improve solute redistribution, and refine solidification microstructures [7–10]. The ECP treatment can also modify the structures of the melt and increase the nucleation rate by increasing the undercooling [11,12]. Previous studies on the undercooling of ECP were performed under the condition of large voltage [13,14] but the undercooling of ECP under low voltage was not studied.

Recently, ECP has been used to optimize the solidification process of immiscible alloys melt [15–17]. Jiang and Zhao [15] found that ECP mainly affects the solidification process by changing the energy barrier for the nucleation of the minority phase droplets (MPDs) in Cu–Bi–Sn immiscible alloys. Ahmed et al. [17] found that, for Pb–Al alloys with Al-rich droplets/particles as the minority phase, ECP could lower the energy barriers for the nucleation of the MPDs and minority phase particles (MPPs), which increases the nucleation rate of the MPDs/MPPs and promotes the formation of Pb–Al alloys with a well-dispersed microstructure.

To observe the effects of ECP treatment on homogenization and solidification structures of alloys, ECP with a pulse voltage of 20 V and different peak current densities was applied to Cu–37.4 wt% Pb alloys during the cooling process. We also compared ECP treatment with the traditional method and the combined method of molten glass purification with cyclic superheating. Furthermore, we elucidated the mechanisms of ECP treatment to weaken the segregation of Pb during solidification based on the

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liquid metal cluster theory and the non-equilibrium diffusion theory.

2 Materials and methods

2.1 Preparation of Cu–37.4 wt% Pb alloys using three different methods

2.1.1 Preparation of Cu–37.4 wt% Pb alloys using the traditional solidification technique

The Cu–37.4 wt% Pb alloys were prepared from high-purity Cu (99.99%) and Pb (99.99%). Briefly, Cu (15 g) and Pb particles (15 g) were well mixed and heated for 3–5 min. When the superheating temperature of the melt reached about 150 K, the samples were cooled at a cooling rate of $10 \text{ K} \cdot \text{min}^{-1}$.

2.1.2 Preparation of Cu–37.4 wt% Pb alloys using molten glass purification and cyclic superheating

The molten glass purification and cyclic superheating were used to purify molten metals. (superheating is a phenomenon that occurs a liquid is heated above its boiling point without actually boiling) Briefly, after the removal of impurities on the surface, Cu particles were placed in a crucible, with the addition of B_2O_3 glass that covered Cu particles. The crucible was heated until Cu particles melted, and then Pb particles (37.4 wt%) were added. When the superheating temperature reached about 150 K, the melt was cooled at a cooling rate of $10 \text{ K} \cdot \text{min}^{-1}$. The cooling curves of the samples were recorded. These procedures were repeated several times until the expected undercooling was achieved. (Undercooling is the difference between the theoretical and actual phase transition temperature of the metal. At high degrees of undercooling, the crystal nucleation rate increases faster than the crystal growth rate, leading to the formation of finer grains [7,8]).

2.1.3 Preparation of Cu–37.4 wt% Pb alloys using ECP treatment

The experimental system includes a customized pulse power supply, a vacuum system, a high-frequency induction heating device, and a temperature measuring system.

Table 1: Parameters of different pulse currents

Samples	Current peaks (A)	Voltages (V)	Pulse widths (μs)	Current frequencies (Hz)
a	800	27	20	30
b	1,000	33	20	30
c	1,200	40	20	30

To reduce heterogeneous nucleation, a customized boron nitride conductive electrode (chemical composition: $\text{BN} + \text{TiB}_2 + \text{AlN}$) was developed and connected to the molybdenum (Mo) electrode with thermal conductivity of $100 \text{ W} \cdot (\text{mK})^{-1}$. High-purity Cu (99.99 wt%) and pure Pb (99.99 wt%) were mixed at a ratio of 68.6:37.4 (Cu:Pb in wt%), and the mixture was placed in a cylindrical boron nitride crucible (7.5 mm in diameter and 30 mm in length), with the addition of B_2O_3 glass. The crucible was evacuated to 10^{-3} – 10^{-4} Pa. When the electrode contacted with the molten metal horizontally, the ECP was applied. The samples were cyclically overheated to 1,200 K for 5 min under Ar atmosphere. The pulse width of 20 μs was used to avoid the generation of joule heat by ECP treatment. During the slow cooling stage, the pulse power was cut off. To compare the effects of ECP treatment on the solidification microstructure of Cu–Pb alloys, the samples were treated with different pulse currents (Table 1). The cooling curves of the samples were also recorded.

2.2 Thermal analysis of Cu–Pb alloys using differential scanning calorimetry (DSC)

Thermal behaviors of Cu–Pb alloys were analyzed on a TGA/DSC1 synchronous thermal analyzer (Quaintest, FL, USA) at a rate of $10 \text{ K} \cdot \text{min}^{-1}$ over a temperature range of room temperature to $1,600^\circ\text{C}$, one cycle for each specimen. The cube alloy specimen had dimensions of $4 \text{ mm} \times 4 \text{ mm} \times 4 \text{ mm}$, and the weight of the specimen was about 25 g. During the cooling of the melt, the melting point was measured by a thermocouple, and the degree of undercooling was calculated by subtracting the phase transition temperature from the theoretical phase transition temperature.

2.3 Metallographic examination

The 10 mm specimens were obtained from solidified samples and polished for metallographic examination. The etching

reagent was composed of 80% anhydrous alcohol, 10% hydrochloric acid, and 10% w/v ferric chloride. The microstructures of Cu–Pb alloys were observed using scanning electron microscopy (SEM) (JSM6510, JEOL, Tokyo, Japan) along the centerline of the specimen.

3 Results

3.1 Solidification microstructure of Cu–Pb alloys

To test whether ECP treatment could refine the grain structures of Cu–Pb alloys during solidification, we compared the microstructures of Cu–Pb alloys prepared by the traditional solidification technique and the combined method of molten glass purification and cyclic superheating (Figure 1). The alloys prepared by the traditional solidification technique had coarse dendrites of the $\alpha(\text{Cu})$ phase and unidirectional solidification structure, with the large Pb phase distributed between $\alpha(\text{Cu})$ dendrites (Figure 1(a)). In contrast, the alloys prepared by the combined method of molten glass purification and cyclic superheating exhibited finer microstructures, smaller spaces between Cu dendrites, and more homogeneous distribution of the Pb phase (Figure 1(b)), suggesting that the combined method could greatly improve the uniformity of Cu–Pb alloys. However, in Figure 1(c), there were larger segregated Pb particles in Cu–Pb alloys possibly due to the collision and coagulation of Pb.

Rapid solidification of alloys at high undercooling can reduce heterogeneous nucleation by maintaining liquid metal at tens to hundreds of degrees below the

liquidus temperature. In this study, the changes in microstructures might be explained as follows. At the undercooling of less than 112 K, the abrupt release of latent heat-induced rapid nucleation and growth of the $\alpha(\text{Cu})$ phase, which immediately wrapped the Pb phase in Cu dendrites to avoid Pb segregation. Over a certain range of undercoolings, the increasing undercooling might cause partial recalescence of $\alpha(\text{Cu})$ dendrites. In this case, the Pb phase could be trapped between those remelted $\alpha(\text{Cu})$ dendrites, further reducing the segregation of the Pb phase. However, once the undercooling was higher than 150 K, the liquid phase separation could cause collision and coagulation of Pb droplets, leading to the segregation of the Pb phase.

A schematic of the cooling curve of Cu-alloys at different undercoolings was shown in Figure 2. At the undercooling of $\Delta T = 112$ K, there was one single recalescence event in the solidification of Cu–Pb alloys. In contrast, at the undercooling of $\Delta T = 150$ K, there were double recalescence events in the solidification of the alloy. The cooling curves further demonstrated our explanation for the microstructural evolution of Cu–Pb alloys during solidification.

3.2 Effects of ECP treatment on structural evolution of Cu–Pb alloys during solidification

The microstructures of Cu–Pb alloys after different ECP treatments are shown in Figure 3. When $I = 800$ A (Figure 3(a)), Cu–Pb alloys possessed a relatively homogeneous microstructure, in which $\alpha(\text{Cu})$ dendrites with tiny primary arms grew in different orientations and the Pb phase

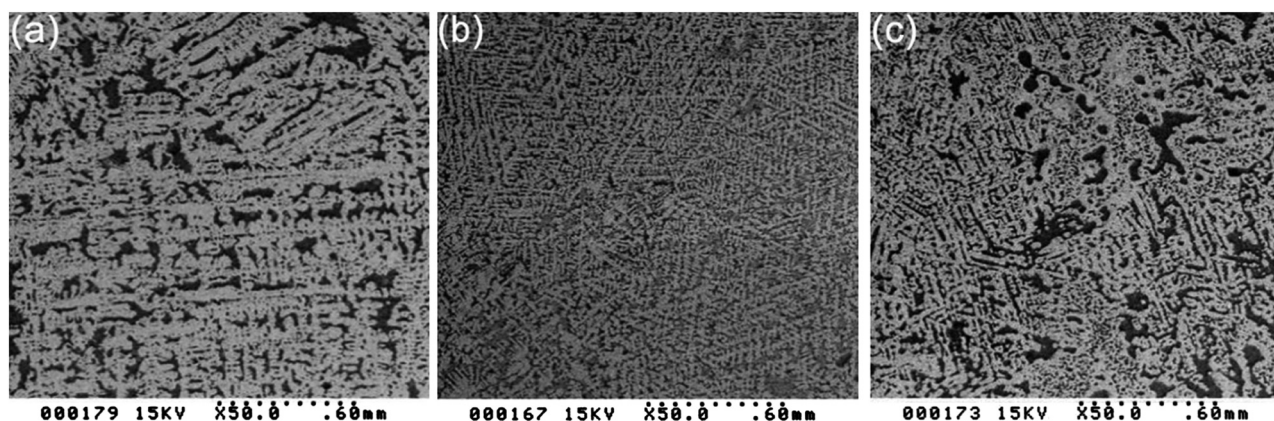


Figure 1: Microstructures of Cu–37.4 wt% Pb monotectic alloys at different undercoolings: (a) $\Delta T = 20$ K, (b) $\Delta T = 112$ K, and (c) $\Delta T = 150$ K.

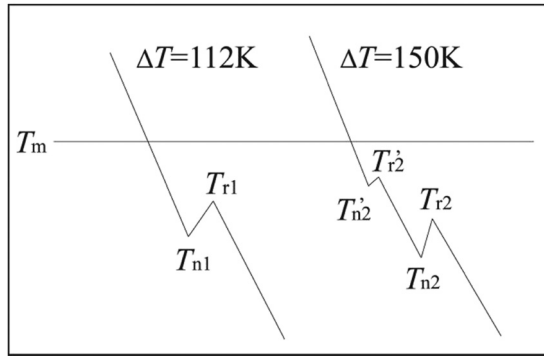


Figure 2: Cooling curves of Cu–37.4 wt% Pb alloys at different undercoolings.

was homogeneously dispersed in $\alpha(\text{Cu})$ dendrites without visible macro-segregation. This result suggests that ECP treatment could improve the microstructural homogeneity in Cu–Pb alloys. When $I = 1,000 \text{ A}$ (Figure 3(b)), $\alpha(\text{Cu})$ dendrites had much shorter primary arms, smaller spacing, and a more homogeneously distributed Pb phase. This indicated that ECP treatment further refined the microstructures of alloys. However, when $I = 1,200 \text{ A}$ (Figure 3(c)), the $\alpha(\text{Cu})$ phase was transited from dendrites to flocculus, and the Pb phase was dissociated and coagulated in $\alpha(\text{Cu})$ dendrites. Moreover, small Pb particles were found in the Cu matrix due to solute trapping. This suggested that ECP treatment could cause some damage to the microstructural evolution of the alloys during solidification.

Figure 4 shows the heating and cooling behaviors of Cu–Pb alloys with or without ECP treatment. Based on the cooling curve (Figure 4(b)), the undercoolings of Cu–Pb alloys with different ECP treatments were determined (Table 2). Compared to the combined method of molten glass purification and cyclic superheating, ECP treatment could refine the solidification structure

of Cu–Pb alloys by reducing the segregation of the Pb phase at similar undercoolings. For example, Cu–Pb alloys prepared by molten glass purification and cyclic superheating at $\Delta T = 112 \text{ K}$ (Figure 1(b)) and $I = 1,000 \text{ A}$ (Figure 3(b)) had similar solidification structures.

By comparing the solidification structures of Cu–Pb alloys prepared under two conditions (Figure 1(c) ($\Delta T = 150 \text{ K}$) vs Figure 3(c) ($I = 1,200 \text{ A}$, $\Delta T = 163 \text{ K}$)), it is found that two alloys had similar undercoolings and fine grain structures. The microstructure of Cu–Pb alloys with ECP treatment had a smaller Pb phase, homogeneous distribution of Pb in the Cu matrix, and slight segregation of Cu dendrites. The results suggested that ECP treatment could reduce the movement of Pb in the Cu matrix and minimize the segregation and condensation of the Pb phase in $\alpha(\text{Cu})$ dendrites.

4 Discussion

4.1 Effects of ECP treatment on the undercooling of alloy melts

After melting, the molten alloy contains many clusters of metal atoms with certain magic numbers [18]. These clusters are different in size, charge, and mass. Upon applying ECP, these clusters could collide with each other by various forces, such as instantaneous electrostatic force, Lorentz force, and viscous force. The strength of these forces varies with different charges and mass of the clusters. If the kinetic energy of two clusters is greater than the repulsive energy, they could be bound together. At the same time, large clusters might be polarized.

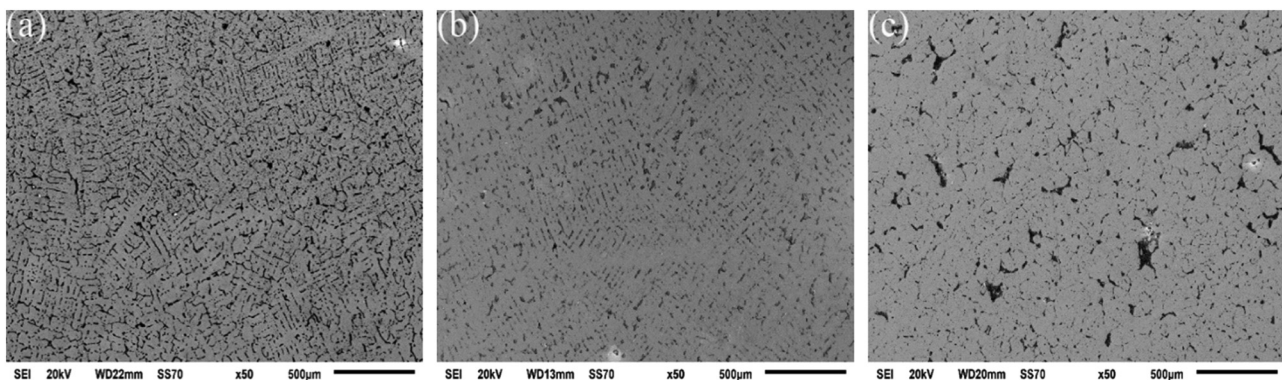


Figure 3: Changes in solidification microstructures of Cu–37.4 wt% Pb alloys with different ECP treatments: (a) $I = 800 \text{ A}$, (b) $I = 1,000 \text{ A}$, and (c) $I = 1,200 \text{ A}$.

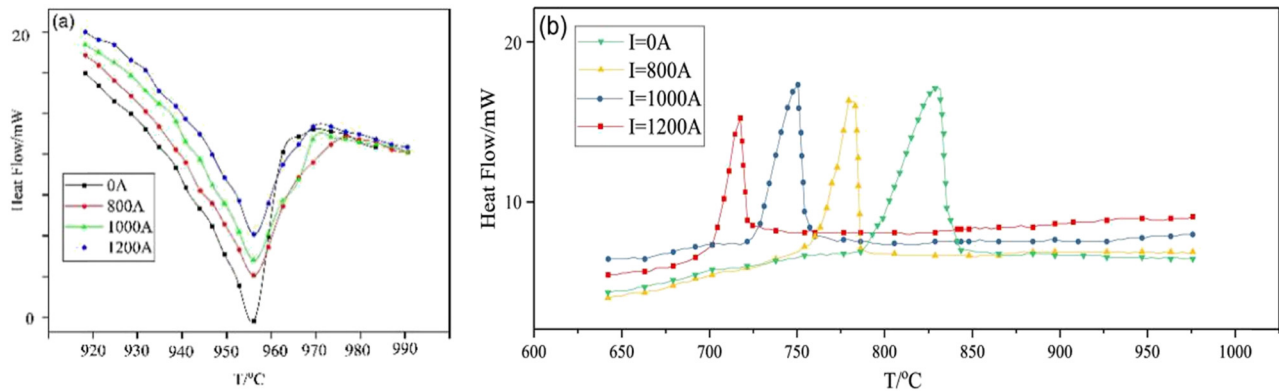


Figure 4: (a) Heating curves and (b) cooling curve of Cu–37.4 wt% Pb alloys with different ECP treatments.

Table 2: Undercoolings of Cu–37.4 wt% Pb alloys with different ECP treatments

		<i>I</i> (800 A)	<i>I</i> (1,000 A)	<i>I</i> (1,200 A)
Undercoolings (K)	24.6	120.1	137.7	163.2

The polarized clusters could be broken by different electrostatic forces to generate smaller colloidal clusters. In addition, the movement of electrons could reduce the local electron density on charged clusters, resulting in the Coulomb explosion and the collapse of stable clusters. Therefore, the effects of ECP treatment might be explained as follows. The pulsed electric field could break larger atomic clusters apart into smaller ones, which increased the undercooling required for small clusters to grow and reach the critical nucleation radius.

Based on the Miedema model [14], the activity can be calculated using equation (1):

$$\ln \gamma_i = \frac{\alpha_{ij}}{RT} \left[\Delta H_{ij} + (1 - x_i) \frac{\partial \Delta H_{ij}}{\partial x_i} \right], \quad (1)$$

where γ_i is the activity coefficient, ΔH_{ij} is the mixing enthalpy, and x_i is the molar volume fraction. The DSC results (Figure 4(b)) showed that the latent heat of fusion L_m decreased when the ECP was applied. Under the same pressure, the mixing enthalpy of the alloys is equal to the latent heat of fusion: $\Delta H_p = L_m$ [19]. Therefore, ECP treatment could significantly decrease the mixing enthalpy, leading to the decreased activity coefficients of Cu and Pb in the melt. The activity of the melt reflects its ability to participate in the reaction. In addition, ECP treatment could reduce the number of dissociated atoms but increase the number of Cu–Pb clusters in the melt. Therefore, ECP could reduce the segregation of the Pb phase in Cu–Pb alloys during solidification.

4.2 Effects of ECP treatment on non-equilibrium diffusion of solute particles

Heat treatment is a non-equilibrium slow diffusion process to refine the microstructures of alloys. The migration of Pb atoms in the matrix needs to overcome the lattice energy barrier. The energy barrier for the solid–solid phase transition mainly consists of interface energy and deformation energy. During solidification, the high temperature could facilitate more solute atoms to overcome the energy barrier to diffuse in the matrix of the alloys. At the same time, due to the effect of instantaneous discharge, ECP treatment could enhance the lattice vibration of atoms from the equilibrium position, thereby reducing the absolute value of the energy barrier ($\Delta E > \Delta E'$). Based on the diffusion model and the nucleation theory of the solid-state phase transition [20], the free energy (ΔG) for phase transition was expressed as equation (2):

$$\Delta G = -n\Delta G_V + \eta n^{2/3}\gamma + nE_s = -n\Delta G_V + \Delta E. \quad (2)$$

The free energy $\Delta G'$ for phase transition under ECP treatment was expressed as equation (3):

$$\Delta G' = -n\Delta G_V + \eta n^{2/3}\gamma + nE_s = -n\Delta G_V + \Delta E' \quad (3)$$

Based on the analysis above, $\Delta G'$ was less than ΔG ($\Delta G' < \Delta G$). Therefore, ECP treatment increased the absolute value of the driving force for phase transition and accelerated the grain-boundary diffusion of Pb. According to the vacancy diffusion mechanism, the jump frequency Γ of Pb atoms in the Cu matrix was given as [21]:

$$\Gamma = Z \cdot P_v \cdot \omega, \quad (4)$$

where Z is the number of the nearest equilibrium positions of the atoms during diffusion; P_v is the probability that the nearest equilibrium position is empty; ω is the probability that diffused atoms jumped into a vacancy site.

In the Cu matrix, Z and P_v can be regarded as constants. Let the vibration frequency of Pb atoms in the direction of the closest free space position be γ and the probability that an atom can cross the energy barrier is $\exp\left(-\frac{\Delta F}{RT}\right)$, the value of ω can be obtained using equation (5):

$$\omega = \gamma \exp\left(\frac{\Delta F}{RT}\right), \quad (5)$$

ECP treatment decreased $\Delta F'$ and increased the value of ω . When the value of ω was substituted in equation (4), Γ increased. Therefore, ECP treatment could allow more Pb atoms to diffuse into the Cu matrix in a short period of time, thus increasing the solid solubility of Cu–Pb alloys and reducing the segregation of Pb in the alloys during solidification.

5 Conclusion

- (1) Compared to the combined method of molten glass purification and cyclic superheating, ECP treatment could significantly refine solidification microstructures of Cu–37.4 wt% Pb alloys at the same undercoolings, leading to more homogeneous distribution of the Pb phase in the Cu matrix.
- (2) ECP treatment could increase the undercooling of Cu–Pb alloy melt by breaking large atomic clusters into small clusters. The increased undercooling facilitated small clusters to collide and reach the critical nucleation radius.
- (3) ECP treatment could enhance the diffusion of the Pb phase in the melt and reduce the segregation of the Pb phase in $\alpha(\text{Cu})$ dendrites.

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Conflict of interest: The authors declare that they have no conflicts of interest.

Data availability statement: Informed consent has been obtained from all individuals included in this study.

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