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Homogeneous Hypermonotectic Alloy Fabricated by Electric-Magnetic-Compound Field Assisting Solidification

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Abstract

The Zn-30wt.%Bi alloys are solidified under different Electric-Magnetic-Compound fields. Results show that a homogeneous solid structure can be achieved when the magnitude of Electric Magnetic Body Forces (EMBF, caused by AC currents interacting with static magnetic field) is 85N/cm³ and the frequency is 50Hz. This is the first time obtaining a homogeneous hypermonotectic alloy by bulk solidification at a relative low cooling rate, 25K/min. The corresponding physical simulations are performed, which reveal that EMBF can mix the layered melt and slow down the droplet motion. Moreover, two physical models are proposed to illustrate how EMBF reduce the droplets' velocities.

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Keywords: Hypermonotectic alloy; Electric-Magnetic-Compound (EMC) field assisting solidifiction; Electric Magentic Body Forces (EMBF)

1. Introduction

Monotectic alloy, particular the hyper one, is one of the ideal candidates for fabricating *in situ* composite materials because the elements it contains have huge physical-chemical property differences [1]. However, this huge property difference blocks the application of monotectic alloy due to the desired homogeneous structure is hard to obtain via the conventional casting. Although the homogeneous monotectic alloys can be achieved by some other methods [2-8], powder metallurgy [9] for instance, casting has its unique appeal to the industry because it is economical and high efficiency.

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To achieve this goal, the solidification behavior of monotectic alloy is worthy to know. Fortunately, massive investigations have been made on understanding how the monotectic melt behaves during cooling [10-13], and a widely accepted view has been reached. Choosing a binary hypermonotectic system as an example, Fig. 1 illustrates what such system experiences from a relatively high temperature to the room temperature. Two elements are entirely miscible at liquid state when the temperature is much higher than the upper line of liquid-liquid immiscible gap after homogenization for a certain time [14]. By cooling the melt into the immiscible region, the melt begins to separate because the inter-atomic force between the same elements is stronger than that between the different ones for the hypermonotectic system [15-17]. Both nucleation and spinodal decomposition are thought to start the liquid separation, but the former is accepted by more people [18]. As reflected by Fig. 1(a), the nuclei grow via diffusion, ripening and collision due to Marangoni migration. After that, the heavier droplets sink down because of the Stokes sedimentation, which causes the layered melt structure before solidification starts. Finally, as shown in Fig. 1(b), the layered solid structure forms through further cooling. This is useless because such structure cannot only enable the material to gain the advances of both elements, but also worse the performance.



Fig. 1. Illustration of solidification process of the hypermonotectic alloy, (a) Quenched structure of Zn-10wt.%Bi alloy showing the collison of two droplets; (b) Layered solid structure of Zn-30wt.%Bi alloy fabricated by casting.

It can get from the solidification behavior of hypermonotectic alloy that the homogeneous solid structure may be achieved if the layered melt structure can be avoided. In fact, several attempts have been made such as mechanical stirring during solidification [19] and super-rapid solidification [20]. However, the ideal structure has not been obtained yet because the mechanical stirring does not work when the solid fracture is high and the super-rapid solidification limits the sample size. Here, by simultaneously imposing AC currents to the sample and applying an external static magnetic field we obtain the homogeneous hypermonotectic alloy by bulk solidification at relatively low cooling rate of 25K/min. The basic principle of this method is also stirring the melt during solidification, but such stirring can work through the whole solidification process and there is no limitation on the sample size. To gain more insight of this method, a series of corresponding physical simulations are carried out.

2. Experimental

Zn-30wt.% Bi alloys used in this study were prepared from 4N Bi and Zn elements by an induction furnace filled with argon atmosphere. The samples were prepared individually because it is hard to make the composition constant if they were prepared by cutting from a bulk mother alloy with inhomogeneous structure. The dimensions of the sample were 15mm in diameter and 20mm long. The experimental device that can realize the Electric-Magnetic-Compound (EMC) field assisting solidification had been detailed described in Ref. [21]. Briefly, it consists of a resistance furnace and control system, a sample holder and power supplier, and a superconducting magnet. All the elements involved in this device were nonmagnetic materials for avoiding any impacts on the magnetic field uniformity. The furnace was controlled by a PID temperature control system with the precision of ± 0.1 K. The

superconducting magnet was supplied by Oxford instrument Ltd., which can provide a vertical static high magnetic field up to 14T with the controlling precision of ± 0.0001 T. The AC currents flowing through the sample were generated by an AC power supplier with adjustable current intensity from 0 to 80A and frequency from 0 to 10000Hz. During experiment, the sample was firstly heated to 700°C and hold for two hours homogenization, and then the external magnetic field and AC currents were switched on simultaneously just before the cooling stared. The experiments were conducted under different magnetic field flux intensities and AC currents densities, but the cooling rate was kept unchanged at 25K/min. The samples' longitudinal structures were examined by the optical microscopy after standard metallographic treatment.

According to the similarity theory, the similarity of geometry, physics, and the initial and boundary conditions should be met to ensure the physical simulation's representativeness. Generally, the simulation is thought to be correct if the similarity of main effect occurring in the experiment [22] can be realized because meeting all three similarity requests is hard in most of the time. For the EMC field assisting solidification of hypermonotectic alloy, EMBF in the melt that caused by interaction of AC currents and static magnetic field is the main effect. To simulate the EMBF, a model system containing $CuSO_4$ electrolyte and silicone oil was chosen because the $CuSO_4$ electrolyte is immiscible with silicone oil and its electric conductivity permits the AC currents flow through and thus can interact with the applying magnetic field, generating the EMBF. Table 1 gives the physical properties of $CuSO_4$ electrolyte, silicon oil, Zn and Bi melts respectively.

Table 1. Physical properties of CuSO ₄ electrolyte, silicon oil, Zn and Bi melts.				
	Conductivity (µS/m)	Dynamic viscosity (Pa·s) 10 ⁻³	Density (Kg/m ³)	Melting temperature (°C)
CuSO ₄ electrolyte	1.96	1.03	1.05	
Silicon oil	<1.7×10 ⁻⁸	0.96	0.96	
Zn melt	2.67×10^{6}	1.98	7.14	419.5
Bi melt	7.81×10 ⁵	1.38	9.80	271.3



Fig. 2. Schematic and photo of the physical simulation apparatus.

The schematic and photo of the physical simulation apparatus are shown in Fig. 2, which consists of an electromagnet, a model cell and an AC power supplier. The electromagnet was cooled by water and can provide an adjustable vertical magnetic field up to 1T in a 50mm high air gap at room temperature. The layered CuSO₄ electrolyte and silicone oil were sealed in an acrylic tube with 45mm inner diameter and 60mm long by the copper electrodes with rubber stoppers at two ends. This was the so-called model cell. The AC power supplier can provide an adjustable current intensity from 0 to 100A and frequency from 0 to 10000Hz with the precision of $\pm 0.1A$ and $\pm 1Hz$ respectively. Moreover, a needle was mounted at the bottom of the acrylic tube to release the silicon oil droplet, which was used to investigate the influence of EMBF on the droplet motion. All the physical simulations were recorded by a CCD camera, which permits us analyze the process frame (1/24 second) by frame.

3. Experimental Results

3.1. Influence of EMBF magnitude on the homogeneity of hypermonotectic alloy

Applying EMC field leads to the direction alternating Lorentz forces in the melt due to the interaction of imposing AC currents flowing through the sample and applying static magnetic field. This is a body force because its unit is, N/cm³, equaling to the gravity density's [23]. Such direction alternating Lorentz forces are named Electric Magnetic Body Force (EMBF) to emphasize its particularity in the present study. Considering the AC currents are orthogonal to the static magnetic field, the modulus of $|B \times J|$ is regarded as the EMBF magnitude here.



Fig. 3. Longitudinal structure of Zn-30wt.% Bi alloys solidified under different EMBF magnitudes with fixed frequency of 50Hz and cooling rate of 25K/min: (a) 0N/cm³; (b) 51N/cm³; (c) 57N/cm³; (d) 85N/cm³; (e) 91N/cm³; (f) 102N/cm³.

Fig. 3 shows the longitudinal structure of Zn-30wt.%Bi alloys solidified at fixed cooling rate of 25K/min under different EMBF magnitudes with fixed frequency of 50Hz. Without any treatment, a typical layered solid structure (Fig. 3(a)) is obtained by conventional bulk solidification, where the dark phase at the bottom is Bi (heaver) and the light phase at the top is Zn. It has known that formation of such structure is in accordance with the solidification behavior of hypermonotectic alloy introduced above. Switch on the EMC field, a 51N/cm³ EMBF distorts the layered structure. As shown in Fig. 3(b), it can see that some Bi phases appear at the top of the sample. This suggests the existence of melt motion during solidification, and the melt motion produced by the 51N/cm³ EMBF must not be severe enough to homogeneously mix the two immiscible melts. Increasing EMBF to 57N/cm³ provides a more homogeneous structure as shown in Fig. 3(c), but there is yet a Bi phase free region existing at the very top of the sample. This indicates that the severer melt motion has been triggered by the 57N/cm³ EMBF, and the much more homogeneous melt can be expected under stronger EMBF. Considering so, EMBF is increased to 85N/cm³, 91N/cm³ and finally 102N/cm³. It can see from Fig. 3(d) that the entirely homogeneous structure is achieved when the EMBF is 85N/cm³, but the degree of structure homogeneity decreases with further increasing EMBF as reflected by Fig. 3(e) and 3(f). Based on these experimental results, it can confidently conclude that the homogeneous hypermonotectic alloy can be achieved by the EMC field assisting solidification at even low cooling rate, but only an optimal condition can provide the entirely homogeneous structure.

3.2. Influence of EMBF frequency on the homogeneity of hypermonotectic alloy

The EMBF frequency is the other key parameter in the EMC field assisting solidification, its effect is investigated with fixed EMBF magnitude of 85N/cm³ that the optimal value found in section 3.1. It is worthy to point out that EMBF frequency is the same as the imposing AC current because the applying external magnetic field is static. Fig. 4 shows macro- and micro- structures of Zn-30wt.%Bi alloys solidified at fixed cooling rate of 25K/min under different EMBF frequencies. Similar to the change tendency of structure homogeneity with the EMBF magnitudes, low EMBF frequency (20Hz) can only distorts the layered melt structure but not mix it. The

entirely homogeneous structure is achieved when EMBF frequency is 50Hz, and the 500Hz EMBF cannot prevent the formation of layered structure. Magnifying regions marked by the white rectangles in Fig. 4(a) to 4(c), it can find that the shape of Bi droplets is irregular under low EMBF frequency (<50Hz) and is almost rounded under high frequency EMBF. The irregular shape of Bi droplets suggests that the mix induced by low frequency EMBF in the melt is intensive, and the nearly rounded Bi droplets embedded in Zn matrix reveals that the melt motion is too mild to break through the interfacial tension restriction of Bi melt under high EMBF frequency. This can be attributed to the decreased effectiveness of EMBF caused by the high frequency. Thereby, the inefficient stir cannot mix or even distort the layered melt. It must notice that, except the EMBF magnitude, there is also an optimal EMBF frequency for achieving the entirely homogeneous structure by the EMC field assisting solidification.



Fig. 4. Macro- and Micro- structure of Zn-30wt.% Bi alloys solidified at fixed cooling rate of 25K/min under different EMBF frequencies: (a) 20Hz; (b) 50Hz; (c) 500Hz.

4. Physical simulation

4.1. Influence of EMBF on mixing the layered liquid structure



Fig. 5. Images of the liquid structures under different EMBF magnitudes with fixed frequency of 2Hz: (a) 1.8 N/cm³; (b) 2.39 N/cm³, and the solid structures they may form are respectively shown in (c) and (d). (e) The average diameter of silicon oil droplets obtained under different EMBF magnitudes.

To get deeper understand how the homogeneous hypermonotectic alloy achieved by the EMC assisting solidification, a series of physical simulations were made in terms of the similarity of main effect occurring in the experiments that generating EMBF in the layered melt. Fig. 5(a) and 5(b) are the images of the liquid structures under different EMBF magnitudes, and the subscript 1 and 2 respectively denote the EMBF orientating inward and outward of the paper. Moreover, the solid structures that may obtain from these liquid structures are shown respectively in Fig. 5(c) and 5(d). It can see that the layered liquid waves when a 1.80 N/m³ EMBF is applied and the interface between the CuSO₄ electrolyte and silicon oil (indicated by the vellow solid/dotted parallelogram) tilts from one side to the other when the EMBF direction changes. However, the layered structure remains unbroken. It should be easy to image that the layered solid structure as shown in Fig. 5(c) must form from the melt structure similar to the one shown in Fig. 5(a). Increasing EMBF to 2.39 N/m³ breaks the layered liquid structure, and the irregular silicon oil droplets are embedded in the $CuSO_4$ electrolyte as shown by Fig. 5(b). It therefore can be expected that the homogeneous solid structure as shown in Fig. 5(d) could form with the melt structure like this. Further, how the layered liquid behaves under stronger EMBF was also investigated, and it found that much more homogeneous liquid structure can be achieved and the average diameter of silicon oil droplets decreases with EMBF as indicated by the curve in Fig. 5(e). This can explain why the solid structure homogeneity increases when the EMBF raises from 57N/cm³ to 85N/cm³ as shown in Fig. 2(c) and 2(d).



Fig. 6. The average diameter of silicon oil droplets obtained under different EMBF frequencies.

The influence of EMBF frequency was investigated by means of physical simulation as well. Similar to the experimental results presented in section 3.2, the layered liquid structure can only be distorted, tilting to one side for instance, but not broken by the very low or high frequency EMBF. Correspondingly, the layered solid structure should be obtained. Specific to the present physical simulation, the layered liquid structure remains unbroken under 1Hz and 100Hz and is homogeneously mixed under the frequency in-between. For the cases that layered liquid is mixed, the average diameter of silicon oil droplets are measured and plotted as a function of EMBF frequency in Fig. 6. It can find that the silicon droplets' size firstly decreases to a minimum value and then increase with the continuously increasing EMBF frequency. This perfectly matches with the conclusion made from the experiments that an optimal EMBF frequency exists for achieving the most homogeneous hypermonotectic alloy.

4.2. Influence of EMBF on the droplet motion

In terms of the introduction on the solidification behavior of hypermonotectic alloy, the motion of minority phase droplets plays a crucial role in forming the layered structure, and this was also thought to be affected by the EMBF. To simulate the droplet motion, a needle was mounted at the bottom of the acrylic tube to release the silicon oil droplet. Dividing the moving distance (*L*) of droplet, which can be measured through the images taken at the moment (N seconds) just after the droplet detached and 1/24 after as illustrated in Fig. 7(a), by 1/24 second, the droplet's velocity can be calculated. The calculated velocities of silicon oil droplets are plotted as a function of EMBF magnitude in Fig. 7(c). It can find that the droplets' motions are dramatically slowed down by the magnitude

increasing EMBF. Moreover, it is found that droplets' moving direction can be changed by the sufficient strong EMBF (stronger than 2.5N/cm³ for this simulation system) as shown in Fig. 7(b). Slowing down the motion velocity can efficiently weaken the collision between droplets that dramatically suppresses its growth. This impedes the liquid separation and then facilitates achieving the homogeneous structure.



Fig. 7. Images of the silicon oil droplet motions under different EMBF magnitudes with fixed frequency of 2Hz: (a) 2.14N/cm³; (b) 3.38N/cm³. (c) The curve of droplets' velocities plotted versus different EMBF magnitudes.

5. Discussions

It has been known, for hypermonotectic alloy, that the liquid separation of uniform melt during cooling is triggered by nucleation, and then the nuclei grow to droplets through diffusion, ripening and further increase its size by collision due to its own motions (Maragoni migration or Stokes sedimentation). Considering the EMBF acting on the minority phase droplet, there are two probable effects may reduce its velocity and thus facilitate achieving the homogeneous structure. One is breaking the droplet into small pieces using EMBF's direction alternating characteristic, and the other is changing its moving path.



Fig. 8. Illustration of how EMBF break the droplet into small pieces: (a₁) the EMBF acting on the droplet; (a₂) the compression and tension of droplet by the EMBF; (a₃) the droplet is broken into small pieces with irregular shape; (a₄) the solid structure contains irregular shape Bi phase. Explanation of how EMBF change the droplet's moving path: (b₁) the droplet sinks down along a straight path in the case of no EMC field; (b₂) the droplet moves along a Z-like path due to its direction is changed by the EMBF, (v is the assumed sinking velocity of the droplet).

Fig. $8(a_1)$ to $8(a_3)$ illustrate how the EMBF break a droplet into small pieces. Switch on the EMC field, EMBF will be generated by the interaction between imposing AC currents and applying static magnetic field. These forces can act on all the conducting substance, so that the minority phase droplet should be subjected to the EMBF as shown in Fig. $8(a_1)$. Such EMBF can compress or tense the droplet because its direction alternates with time (Fig. $8(a_2)$), and finally, the strong enough compression or tension will break the droplet into pieces. These small pieces are shape irregular as shown in Fig. $8(a_3)$. This can explain why the shape of Bi droplets is irregular under sufficient strong EMBF as shown in Fig. $8(a_4)$. Moreover, it is worthy to mention that the smaller droplet has slower velocity which retards the droplet collision and is benefit to achieve the homogeneous structure.

Fig. $8(b_1)$ and $8(b_2)$ explain how the EMBF change the droplet's moving path. Without the EMC field, droplets should sink down (or float up) almost along a straight path because of the big density difference between two elements, liking the case shown in Fig. $8(b_1)$. As revealed by the physical simulation (Fig. 7(b)), the droplet's moving direction can be shifted by the sufficient strong EMBF, and this results in a Z-like moving path as illustrated in Fig. $8(b_2)$. It has been known that the effective friction coefficient is higher if the droplet moves along the non-straight path rather than a straight one [22], so that the Z-like moving path reduces the droplet's velocity. Additionally, the moving distance of a Z-like path is much longer than a straight one if the distance between the start and end points is constant. The lengthened moving distance makes the droplet taking more time to reach the bottom of sample or collide with the other one. This provides the possibility to achieve the homogeneous structure at a lower cooling rate. These two effects both suppress the liquid separation and thereby facilitate achieving the homogeneous structure.

6. Conclusions

A new method to fabricate the homogeneous hypermonotectic alloy was proposed that the EMC field assisting solidification. The optimal process condition for achieving the entirely homogeneous solid structure of Zn-30wt.%Bi alloy was found through the experiments, which was 85N/cm³ EMBF with the frequency of 50Hz. The corresponding physical simulations were conducted to get deep understand of this method, which revealed that the EMBF can mix the layered melt homogeneously and reduce the velocity of minority phase droplets. The former is the precondition for achieving homogeneous solid structure and the latter one suppresses the liquid separation thereby facilitates obtaining the homogeneous melt structure. Moreover, the physical simulation confirmed that the optimal EMBF magnitude and frequency for achieving the entirely homogeneous structure do exist. Based on the experiments and simulations, two physical models were proposed to illustrate how EMBF break the droplet into small pieces and change the droplet's moving path. These two effects are both dedicated to reduce the droplets' velocity.

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