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Liquid phase separating mechanism and preparation techniques of immiscible alloys①

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[Abstract] Immiscible alloys have attracted growing interest for their valuable physical and mechanical properties. However, their production is difficult because of metallurgical problems in which there is a serious tendency for gravity separation in the region of the miscibility gap. So far the study on the liquid separation mechanism is still one of the important projects in the spatial materials science and the spatial fluid science. The studied results about the liquid phase separating mechanism of immiscible alloys are presented, at the same time the preparation techniques of homogeneous immiscible alloys are summarized, and the existing problems and the related researching areas in the future are also pointed out.

[Key words] immiscible alloys; liquid phase separating mechanism; preparation techniques
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1 INTRODUCTION

The binary phase diagrams of immiscible systems all have a miscibility gap in which the original single liquid will decompose into two distinct immiscible liquids within a few seconds. In the normal gravity field, the sedimentation of the heavier phase leads to a serious gravity segregation even a layered structure which has any valuable applications. But many immiscible alloys with homogeneous structure perform particular physical and mechanical properties. For example, they can be used as self-lubricating materials[1], superconducting materials[2], semi-conducting material and electrochemical material[3], contact material[4] and so on.

After 1970's, the development of the aerospace science and technology made it possible to study immiscible alloys in spatial microgravity conditions. So far it is still one of the important projects in the spatial materials science and the spatial fluid science. By now, people have a relatively clear understanding to their liquid phase separating process and the influencing factors[5]. Besides the gravity, a large number of possible additional mechanisms have been identified theoretically which may influence the phase separation. Recently, with the development of the preparation techniques and the need of immiscible alloys' particular properties, the preparation and practical applications of immiscible alloys also attract much attention from researchers. Therefore, this paper will summarize the studies about the liquid phase separating mechanism of immiscible alloys and their preparation techniques, finally point out the existing problems and the related researching fields in the future.

2 STUDY STATUS ON IMMISCIBLE ALLOYS

2.1 Solidification and nucleation characteristics

Fig. 1 illustrates a typical binary phase diagram of an immiscible alloy. The homogeneous liquid L will decompose into the liquids L_1 and L_2 when the temperature crossing the binodal line *mcb* (i.e. the curve of coexistence). On further cooling in the normal gravity field, a serious gravity segregation even the layered structure will arise due to the sedimentation of the heavier phase.

The minority phase is known to form through nucleation and growth. In the early 1960's, Sundquist and Oriani[6, 7] had begun to study the nucleating character of C7H14-C7F14 immiscible system. Their experimental results demonstrated that the critical nucleation under-cooling degree varied with composition. In other words, the needed under-cooling degrees increase with increasing $|x - x_c|$. But when the compositions are near x_c, the under-cooling degrees are near zero. After that, Heady and Cahn[8] again performed the nucleation experiment after carefully measuring the related thermophysical parameters and obtained the same results. The measured results of Perepezko[9] through DTA method first testified the relationship between the under-cooling degree and the composition of Ga-Bi system, as

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shown in Fig. 2. The calculated results of Zn-Pb by ZHAO Jiu-zhou[10] and Al-In by LIU Yuan[11] also presented the same changing trend. At present, this kind of relationship has been accepted by most researchers.

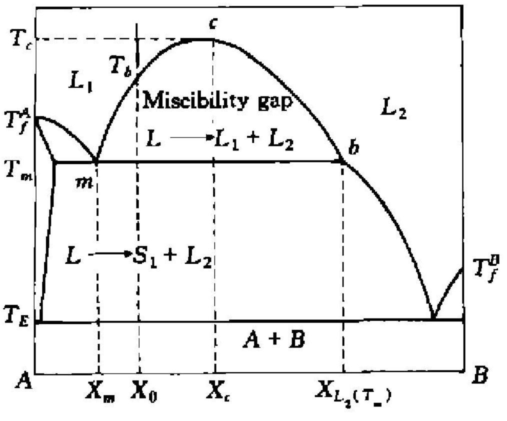

Fig. 1 Typical binary phase diagram of an immiscible alloy

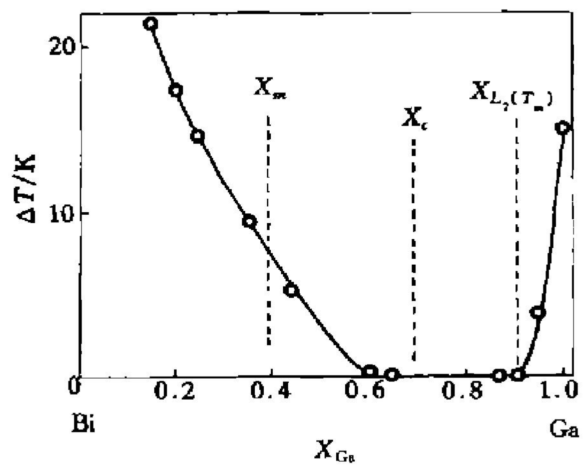

Fig. 2 Measured nucleation undercoolings (ΔT) in Bi-Ga alloys[9]

2. 2 Liquid-liquid phase separation of immiscible alloys

In earlier time, the researcher had the expectation that microgravity conditions should lead to spatially homogenous dispersion of the second phase distributed in the matrix. But it is unfortunately that the initial several experiments[12~14] all showed the metallic dispersions still had massive separation even in space. The failures stimulated intensive theoretical and experimental research on earth and in space to immiscible alloys. In the earlier stage of 1970's, the scientists of America NASA first made some pioneer experiments on Apollo-14, Apollo-16 and Skylab, etc[12~15]. After that, the scientists of Europe Space Agency[16, 17] and Japan Space Agency[18] also performed successively many related researches by utilizing spacecrafts such as rocket. China also made some experiments by the use of recoverable satellite in 1987[19, 20].

Lancy[12], a scientist of America NASA, firstly made some experiments to Zn-Pb on Apollo-14. His study demonstrated that there still existed a serious segregation in Zn-Pb alloy and the cause was thought to be that the phase diagram is maybe inaccurate. But after carefully reviewing the phase diagram of Al-In, the solidification experiments of Al-In performed by Lohberg[13] also obtained the similar segregation structure in which Al is enveloped by a shell of In. While the experiment performed by Potard[14] with the SiC crucible showed a reverse result in which In was enveloped by Al. These two experiments indicate that the wetting ability of the component to the crucible materials is one of the major factors influencing the liquid phase separation.

After avoiding the influence of the crucible materials, Gells et al[15] also got a layered structure of Al-In immiscible alloy under microgravity condition. In this case, it is concluded that Marangoni convection induced by the interface tension gradient due to the temperature gradient in the melt is the prime criminal. These early experiments under spatial microgravity conditions can't present any merits of microgravity and only found, besides the gravity, some other factors influencing the liquid phase separating process of the immiscible alloy.

Fredriksson and coworkers[16] from the Europe Space Agency performed many experiments on Zn-Bi alloy during the flying process of rocket. The experimental results showed that a higher Bi content caused Zn to be enveloped by a shell of Bi-rich phase. But a lower Bi content caused Bi-rich phase to distribute in Zn matrix. In addition, the distribution of Bi rich phase becomes more homogeneous when the cooling rate changes from 3.6 ℃/s to 2.4 ℃/s. It is obvious that the volume fraction of the second phase and cooling rate also have important effects on the liquid separating process. Additionally, they thought that the residual gravity (Stokes motion) and Marangoni migration of the second phase droplets also aggregated the segregation. A higher cooling rate leads to a higher temperature gradient and a serious Marangoni migration of the second phase droplets, correspondingly more serious segregation.

Walter and coworkers[17, 21] made a serials of experiments on eight kinds of Al-based immiscible alloys with In, Bi or Pb additive. Fig. 3(a) shows the directional solidification of Al-In. It is obvious that Marangoni migration of indium droplets leads to its enrichment in the outside of the sample. In addition, by the radial heat-extraction method, they made a radial solidification of Al-9% Pb (in volume fraction) melt in the crucible and the obtained structure is shown in Fig. 3(b). In this case, Marangoni migration of Pb droplets from the outer to the center of the sample is the corresponding cause.

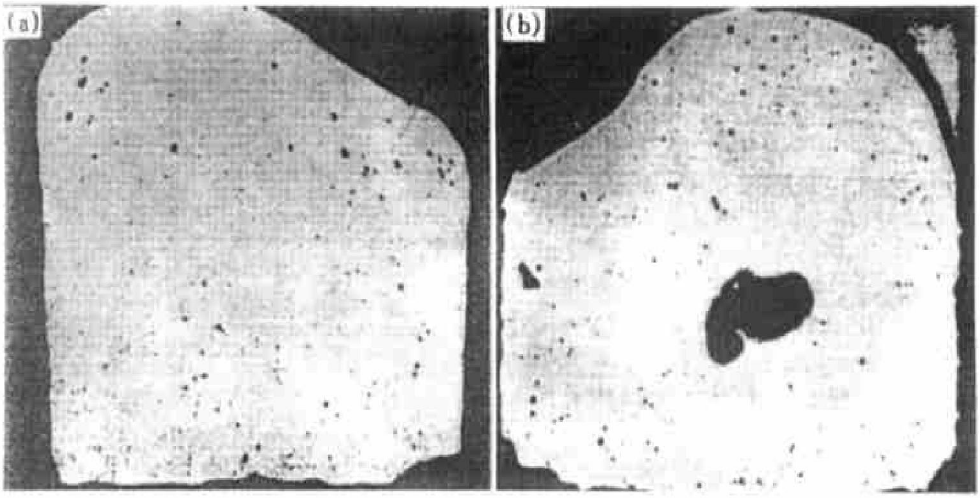

Fig. 3 Effect of Marangoni motion on liquid-liquid separation process[17]
(a) —Al-10% In sample radial solidification from inner to outer; (b) —Al-9% Pb sample radial solidification from outer to inner

The process of Ostwald ripening was studied by Kneinl and Fischmeister[22] in a Space Lab 1 experiment. Otto[23] studied the precipitation of liquid mercury from a supersaturated gallium melt in an automated MAUS facility on board of the Space Shuttle. The dispersion of Hg droplets in Ga could be recorded in situ by X-ray transmission photographs. Fig. 4 shows such X-ray photographs of a cooling cycle[23], first showing clearly the appearance and growth of the droplets. The mercury droplets are in the range of 0.2 to 1.2 mm radius and rise with time. In addition, the calculated results according to diffusional growth are higher than the experimental values especially at a higher cooling rate. One of the possible causes is the additive Marangoni collisions between droplets due to the higher temperature gradient caused by the higher cooling rate.

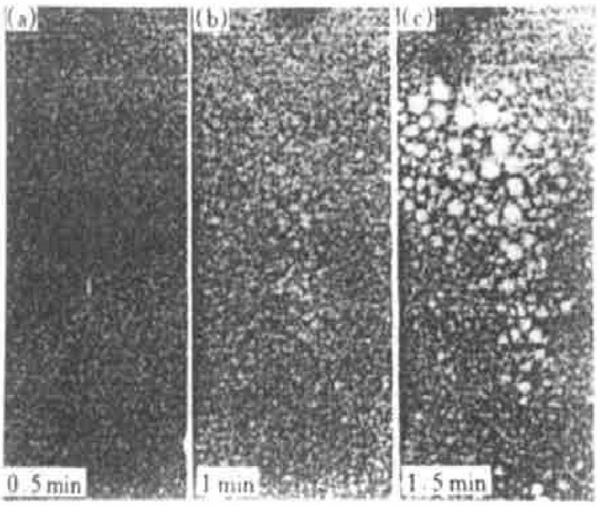

Fig. 4 Precipitation process of mercury droplets from supersaturated Ga(Hg) liquid on cooling into miscibility gap by X-ray transmission photographs[23]

In 1992, Japanese scientists[18] made some experiments on Space Lab-3. After decreasing the temperature gradient in the melt as low as possible, they got homogeneous Al-Pb-Bi cast ingot and studied the effects of the size, distribution and volume fraction of the second phase particles on the superconductivity.

In 1987, China researchers made some solidification experiment on Al-Pb, Pb-Al and Zn-Pb with recoverable satellites[19, 20]. Their studies show that, although the natural convection is excluded under the microgravity conditions, Marangoni convection still exists and thus becomes the major factor influencing the final microstructure. China researchers also studied the effect of interfacial energy on the microstructure of Al-In immiscible alloy on recoverable satellite[24]. The effect of the interfacial energy on the microstructure behaves very prominent, especially in the directional solidification of immiscible alloys[25~27].

These experiments made in the spatial microgravity circumstances indicate that Marangoni migration makes a great contribution to the separation process of immiscible alloys, even though under the normal gravity condition.

Besides in the spatial microgravity conditions, China and Russia researchers had also studied the phase separation of immiscible alloys in the simulated microgravity fields such as dropping tower[28~30] and orthogonal electromagnetic field[31~37] on earth. These studies intensify peoples' understandings to immiscible alloys. So far the following factors have been found to influence the liquid phase separation of immiscible alloys:

1) Nucleation of second phase droplet;
2) Growth-diffusion-convection/diffusion;
3) Stokes motion of the second phase droplet;
4) Interfacial energies;
5) Ostwald ripening;
6) Marangoni migration of the second phase droplet;
7) Concentration of the second phase and the cooling rate;

8) Brownian coagulation;

9) Secondary convection induced by the shape change.

The phase separating process of immiscible alloys included three stages.

① Nucleation stage. When the original melt is cooled down to the miscible temperature, a great number of nuclei or droplets will form quickly in the melt through energy and concentration fluctuation.

② Growth and coarsening stage.

In this stage, the second phase droplets grow up or shrink by diffusion (namely Ostwald ripening). At the same time, they coarsen continuously through collisions including Marangoni and Stokes collision.

③ Sedimentation stage.

When the droplets coarsen up to a considerable value, the sedimentation arises due to the density difference between L_1 and L_2. At the same time, the second phase droplets coarsen continuously by Marangoni coagulation and Stokes coagulation, especially by Stokes coagulation.

3 PREPARATION METHODS OF IMMISCIBLE ALLOYS

Before 1970, people rarely considered the actual applications of immiscible alloys because of the limited understanding to its liquid-liquid phase separation mechanism. Recently, with the development of the preparation techniques as well as the need to immiscible alloys' particular properties, researchers also paid much attention to the preparation and practical applications of immiscible alloys. Brief introductions to these preparation methods are presented as following.

3.1 Powder metallurgy

In the early 1939, some scholars had used the powder metallurgical technology to sinter Pb-Cu immiscible alloy[38]. In 1974, Feder et al[39] put forward a new process—atomization preparing powder plus powder sintering (i. e. RS/PM) in their patent to produce Al-Pb bearing material. After that, this kind of process (RS/PM) becomes the traditional process employed to prepare homogeneous Al-Pb, Cu-Pb and other self-lubricating materials[40, 41]. China also introduced this kind of process to produce Al-Pb bearing material in 1995.

The alloy's properties strongly depend on the sintering processing parameters. The shortcomings of powder metallurgy are the numerous producing procedures and the higher cost. In addition, the powders are easy to be oxidized or contaminated, which will lead to poor coherence between powders.

3.2 Directional solidification

During the directional solidification, because that only a small region before the solidifying front goes into the miscibility gap, the second phase droplets will be trapped soon and a homogeneous microstructure can be obtained.

The studied results[42~45] reveal that many kinds of morphologies can be got, which depends on the cooling rate and the interfacial energies. When L_2 has a poor wetting ability to the solidifying interface, namely $\gamma_{S_1L_2} > \gamma_{S_1L_1} + \gamma_{L_1L_2}$, as the cooling rate rises, the morphologies change from the banded structure in which bands of L_2 particles distribute in the S_1 matrix to the irregular fibrous composite structure in which short fibers or rods of L_2 distribute irregularly in the matrix, and to the particle composite structure in which L_2 particles randomly distribute in the S_1 matrix. When the second phase (L_2) has a good wetting ability to the solidifying phase (S_1), namely $\gamma_{S_1L_2} < \gamma_{S_1L_1} + \gamma_{L_1L_2}$, and the cooling rate is lower, the regular fibrous composite structure in which well aligned and close packed arrangement of L_2 fibers or rods distributing in the S_1 matrix can be obtained. When the cooling rate further rises, the morphologies will change into the particle composite structure. In addition, some other studies[27] also show that for the immiscible systems with a higher miscibility gap, the regular fibrous composite structure tends to form. Inversely, the irregular banded structure or the particle composite structure tends to form. However, up to date, there still has no uniform criterion on the transition between different morphologies.

3.3 Melting and casting under microgravity conditions

3.3.1 Spatial microgravity conditions

The experiments to prepare homogeneous immiscible alloys under the spatial microgravity conditions have been introduced in the previous section. Although the gravitational sedimentation can be eliminated under the microgravity conditions, the influences of other factors, especially the influence of Marangoni migration of the dispersed droplets emerges, so it is still difficult to get homogeneous immiscible alloys.

3.3.2 Simulated microgravity conditions

The Russians firstly used the orthogonal electromagnetic field to simulate the microgravity environment[31, 32]. Chinese ZHAO Jiu-zhou and JIA Jun also used the same method to prepare successfully homogeneous Zn-Pb alloy with a small quantity of Pb[33~37]. Its basic principle is that, in the same electromagnetic field, different electromagnetic force density will generate in different component because of their different electric conductivity (the current direction is perpendicular to the magnetic direction), so an appropriate electromagnetic parameter can be found to make the following equation be satisfied

$$\rho_D \boldsymbol{g} + \boldsymbol{J}_D \times \boldsymbol{B} = \rho_M \boldsymbol{G} + \boldsymbol{J}_M \times \boldsymbol{B}$$

where ρ_D, ρ_M are the densities of second phase and matrix phase, respectively; $\boldsymbol{J}_D$, $\boldsymbol{J}_M$ are the current densities in the second phase and matrix phase, respectively; $\boldsymbol{g}$ and $\boldsymbol{B}$ are the gravitational acceleration and magnetic intensity, respectively. At this time, the electromagnetic force can counteract the weight difference between them and as if the melt is placed in a microgravity field. But unfortunately, Marangoni migration of the second phase droplets and the residual Stokes motion are still not avoidable. In addition, the appropriate electromagnetic parameters are not easy to find.

Besides using orthogonal electromagnetic field, some researchers use dropping tower of tens of meters height to attain the microgravity condition[28~30]. When the crucible containing the uniform melt drops down to a certain position, the melt will solidify at the partial zero-gravity state. But it is also difficult to get homogeneous immiscible alloys.

3.4 Stirring casting

Vigorous stirring can not only disperse the second phase droplets in liquid matrix and prevent the second phase from settling or floating. The resulting dispersion is solidified as quickly as possible in order to minimize the gravitational segregation. Recently this kind of method is primarily employed in production of Al-Pb bearings. The stirring manners generally include three categories, namely mechanical stirring[46~49], ultrasonic stirring[50] and induction stirring[51]. The volume fraction of second phase, stirring speed and cooling rate in the mold are the primary factors influencing the second phase particle size and distribution. The higher the stirring speed is, the wider the range of particle sizes are, the bigger the particles are. The higher the volume fraction of the second phase is, the bigger the second phase particles are. The higher the cooling rate is, the smaller the second phase particles are. The induction stirring can get the best stir-cast microstructure, while the particles in the ultrasonic stir-cast microstructure are generally bigger than that in other two kinds of stir-cast microstructures. This kind of technology is simple and the cost is lower, too. However, there still exists a certain degree of segregation and the second phase particles are frequently bigger and mainly distribute at the grain boundaries.

3.5 Controlled casting

Some people designed a new technique named as controlled casting[52~54] in which a temperature gradient in the opposite direction of the gravity is imported so as to make the second phase droplets do Marangoni migration opposite Stokes sedimentation. The net velocity of the droplets in the melt will be dependent on their sizes. When the size of the droplets is very small, Marangoni migration of the droplets will be predominant. Otherwise Stokes motion will be predominant. When the droplet grows up to a critical size, its net velocity will reach zero. So by controlling the stability of the solidification process, an immiscible alloy ingot with uniform distribution of the second phase particles can be obtained. However, it is still difficult, sometimes impossible to produce homogeneity ingots due to the difficulty in controlling the stability of the solidification process and the sedimentation or floatation of the second phase droplets before they grows up to the critical sizes.

3.6 Rapid solidification

The rapid solidification technique being applied to immiscible alloy is inevitable. It has been recognized that the segregation of the second phase is dependent on the dynamical process (i.e. the growth, the coagulation as well as the movement of the second phase droplets). So if the solidification is so rapid that the second droplets will be entrapped soon by the matrix phase. As a result, homogeneous immiscible alloys with fine dispersion structure can be obtained. The rapid solidification technology is the most promising one and has been paid much more attention than the other preparation methods.

In 1978, Ojha and Chattopadhyay[55] reported the "Gun" rapid solidification preparation of Al-In immiscible alloy and established the possibility of obtaining homogeneous immiscible alloys. After that, researchers employed other rapid solidification technologies such as atomization preparing powder, melt-spinning, planar flow casting to prepare the powders, strips or as-deposited ingots of immiscible alloys[56~59]. The present authors studied the melt spinning process of Al-In alloys[60~62]. These studies show that the rapid solidification method can produce homogeneous immiscible alloys with fine structure. The cooling rate, the composition and the interphase interfacial energies are the major factors influencing the particle size and its distribution.

In order to avoid the shortage—smaller material (line, ribbon or strip, etc) of the substrate cooling technologies such as melt-spinning, gun method and planar flow casting, in recent years, many researchers[63~65] also made many attempts to produce directly bulk immiscible alloys with the spray deposition technology. The as-deposited ingot, with the character of homogeneous distribution of the second phase particles, can be used only after the milling process. In addition, a new type of spray co-deposition process in which two liquid metals are sprayed together from different atomization nozzle has been developed[66]. This method can decrease the melting temperature and save energy.

In addition, the present authors also investigated the solidification of Al-In immiscible alloys in copper mould[11, 67]. For Al-In alloys not more than 30% In in mass fraction, this method can produce sheets not thicker than 4mm without segregation or with slight segregation. Germany researchers[68] developed a continuous cast process in which the uniform melt of immiscible alloy is poured onto a steel substrate moving continuously and solidifies as a thin layer of homogeneous structure. This method can produce self-lubricating bearings that can be used after a simple machining. In addition, Germany researchers[69] also developed another method in which the melt is drawn continuously from a water-cooling copper mould. This kind of method can produce several millimeters to 10mm thick Al-Pb sheets with weak segregation. The above processes used to produce balk homogeneous immiscible alloys have built a sound basis for the practical applications of immiscible alloys.

4 COMPUTER SIMULATION ON SOLIDIFICATION OF IMMISCIBLE ALLOYS

The computer simulation on the solidification microstructure of immiscible alloys is an important embranchment of the researches on immiscible alloys. Essentially, the studies related to the computer simulation on the solidification of immiscible alloys can be divided into two classes: one is called as density dynamic method, the other is called as particle separation method.

4.1 Density dynamic method

The classical method used to deal with collisions and coagulations in dispersed systems is the population dynamical approach first developed by Smoluchowski[70]. Let $f(R, t, \Theta)\,\mathrm{d}R$ be the number density of droplets per unit volume with radius in the range $R+\mathrm{d}R$ at position Θ. $f(R, t, \Theta)$ is named as the radius distribution function. If we consider the common action of the nucleation, the diffusional growth and collisions between droplets, the distribution function then obeys a continuity equation of the following form:

$$\frac{\partial f(R, t, \Theta)}{\partial t} = \frac{\partial I_{\mathrm{hom}}}{\partial R}\Big|_{R=R^*} - \frac{\partial}{\partial R}[v(\Theta, R, t)f(R, t, \Theta)] - \frac{\partial}{\partial \Theta}(uf(R, t, \Theta)) + [\frac{1}{2}\int_0^R W(R_1, R_2)\cdot f(R_1, t)f(R_2, t)(\frac{R}{R_2})^2\mathrm{d}R_1 - \int_0^\infty W(R, R_1)f(R, t)f(R_1, t)\mathrm{d}R_1] \quad (1)$$

where $R_1^3+R_2^3=R^3$, $W(R_1, R_2)$ is the so-called collision volume measured in unit of cubic metres per second; I_{hom}, v and u are the homogeneous nucleation rate, the growth rate and the moving rate of the second phase droplets, respectively. In the right hand of this equation, the first to the fourth term represents all droplets leaving or adding to the radius class R due to the nucleation, the diffusional growth, the movement of droplets and collisions between them, respectively.

There have been many attempts to model at least part of the microstructure evolution in the miscibility gap by using Eqn. (1). But unfortunately, this equation is so complicated[71~85] that it can't be solved analytically or numerically unless simplifying some special conditions or terms before solution. So it can only be used to analyze the microstructural evolution under some special or simple conditions and can't reflect the practical solidification process very well. Although these simplified models based on density dynamic method can explain the experimental results at a certain degree, they can't reflect the real solidification process.

4.2 Particle separation method

It is a new theoretical method put forward by Ratke and Diefenbach[86] to describe the microstructural evolution of immiscible alloys. Its basic calculation procedures are at follows. 1) At the beginning of each time step, first get the temperature field in the sample through measuring or calculating, and coupling it with the solidification dynamics, when a position is cooled down to a temperature when the nucleation starts to occur, calculate the nucleation rate here. 2) After that the diffusional growth, the coagulations including Brownian coagulation, Stokes coagulation and Marangoni coagulation will be calculated. In addition, the concentration field, the supersaturation in the melt and the position of each droplet must be calculated and stored. 3) At the next time step, repeat the above procedure until all of the units solidify completely. 4) Finally, the size and distribution of the second phase particles on the cross-section of the sample will be obtained.

The calculation process of particle separation method is identical with the real solidification process and is a promising method applied to simulate the microstructural evolution of immiscible alloys. However, it also has a shortage that is a larger computation quantity because that we must track and store the positions of large numbers of droplets at any moment. So an improvement to the method is necessary for its practical application.

In the revised particle separation method[11] developed by the present authors, the droplets are divided into different size classes according to their radius and the stochastic collection equation is used to deal with the collisions, so the computation quantity is reduced sharply, which makes the application of the particle separation method become possible. This method can efficiently predict the size and distribution of the second phase particles and has a good guiding function for the production of immiscible alloys. However, the convection in the melt and the pushing action of the solid/liquid front to the second phase droplets have been not considered in this model, so further improvements are necessary.

5 COMMENTS

The particular mechanical and physical properties of immiscible alloys imply their potential applications in industries. However, their practical applications depend upon our knowledge of the liquid phase separating mechanism and the development of the new preparation techniques. Therefore, in the future, the following four aspects should be the major focus. One is the liquid-liquid phase separation mechanism. This part should focus on the computer simulation through establishing theoretical model respecting the real solidification process and physical mechanism. The second is the study on the phase diagram and the thermophysical parameters which are the most important basis for theoretical analysis. However, at present, the available parameters are limited and even inaccurate. The third is the development of the preparation techniques especially the techniques producing bulk homogeneous immiscible alloys, which is the key promoting the industrial applications of immiscible alloys. The fourth is the relationship between the properties and the microstructures.

The present author's research group is now paying its attentions to the numerical simulation of the liquid phase separating process and the microstructural evolution during the cooling process. Now the established numerical model and the developed simulation program by ourselves can predict the size and distribution of the minority phase particles on the cross-sections of the castings solidifying unidirectionally. The further improvements will be made in the future. In addition, the preparation technique, especially preparation of bulk homogeneous immiscible alloys is another studying field. Now we can produce not higher then 4mm thick Al-In alloy sheets[11]. We are sure that, with the development of these studies, in the future materials field, many immiscible systems with excellent properties will found their applications in structural, wear resistant, contact as well as superconducting materials.

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