Effect of Rare-Earth Ce on Macrosegregation in Al-Bi Immiscible Alloys

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Abstract: Liquid phase segregation of immiscible alloys has been investigated for decades. In this work, rare-earth Ce was studied as an additive for Al-Bi immiscible alloys. The addition of Ce restrained liquid phase segregation to obtain a uniformly dispersive microstructure. The experimental results indicated that in situ-precipitated intermetallic CeBi₂ compound acted as an inoculant for the heterogeneous nucleation of the Bi-rich droplets. The Bi-rich droplets nucleated on the CeBi₂ compound surface—a homogenous dispersed microstructure obtained via a heterogeneous nucleation route. We concluded that gravity segregation can be suppressed by the addition of rare-earth Ce.

Keywords: immiscible alloys; rare-earth alloy; liquid–liquid segregation; heterogeneous nucleation

1. Introduction

Immiscible alloys have been investigated as a kind of special metallurgy characteristics alloy [1–3]. In phase diagrams, immiscible alloys have a miscibility gap in the liquid state. When temperature exceeds the immiscibility gap, the binary phases become a uniform liquid phase. The alloys begin liquid–liquid phase separation when temperature is cooled down into the miscibility gap. The growth and motion of droplets are influenced by nucleation, growth, Ostwald ripening, coagulation, Marangoni convection, and Stokes sedimentation [4–6]. The liquid–liquid phase separation results in a segregated microstructure. Immiscible alloys have potential practical applications, especially in advanced bearing materials for their self-lubricating property. Some literature [7,8] has indicated that the excellent self-lubricating performance is dependent on a uniformly-dispersed distribution of the soft phase. However, the potential applications of immiscible alloys have been restricted because of the segregation between matrix and soft phase. To obtain dispersive solidified morphology is an unsolved scientific problem.

Researchers have investigated the solidification mechanism of phase segregation for a long time to obtain homogenous microstructure, whereas the dispersive distribution of a minority phase is still hard to achieve. It is necessary to design new methods to fabricate immiscible alloys with a uniform dispersive microstructure. To control the liquid–liquid phase separation, many experimental methods have been designed, such as rapid cooling [9,10], directional solidification [11,12], high static magnetic field [12,13], and other routes [14–16]. Nevertheless, some methods are hard to apply in industry due to harsh conditions during the experimental procedure. In recent years, the addition of third elements has attracted increasing attention. Some studies [17–20] showed that addition of the third elements has a great influence on liquid phase segregation and the solidification process. It should be noted that it is
an easy operating method and can also be applied in other fabrication methods. This method would effectively retrain liquid phase segregation to obtain immiscible alloys with refined microstructure. Budai and Kaptay [21] and Nagy et al. [22] presented the homogenous microstructure of Al-Cd alloys by in situ precipitating intermetallic Al$_4$Sr compounds. The intermetallic precipitates prefer to exist at the Al-Cd interface and to stabilize the Cd droplets in the Al matrix. Sun et al. [23] studied TiC used as inoculant for the nucleation of Pb-rich droplets. The addition of TiC particles suppressed liquid–liquid segregation and formed a disperedd microstructure. These studies confirmed that the third elements can refine the soft phase of immiscible alloys.

The effect of rare-earth Ce on immiscible alloys has not been reported at present. In the present study, we investigated the effect of rare-earth Ce on the liquid phase segregation of Al-Bi immiscible alloys. Al-Bi immiscible alloys are potential candidates for advanced bearing material if the soft phase is dispersively distributed in the hard phase. The third element additive involves the addition or in situ formation of potent nuclei in the system to promote nucleation events. It is difficult to obtain a uniform dispersion microstructure by the addition of particles, due to wetting of particles in the metal matrix. The in situ intermetallic compounds do have similar crystallographic characteristics with the soft phase. Thus, in situ intermetallic compounds can be used as heterogeneous nucleation sites for the Bi-rich phase, from a wetting point of view. The in situ-precipitated compounds are produced during melting. We also discuss the influence of different concentrations of rare-earth Ce on the solidified microstructure.

2. Experimental Procedure

Al-20% Bi alloys are chosen due to the wide miscibility gap in the phase diagram, shown in Figure 1. The ingots were prepared by melting pure Al (99.99 mass%), pure Bi (99.99 mass%), and Ce (99.5 mass%). An alumina crucible with a diameter of 20 mm and a height of 90 mm was used for melting. The rare-earth Ce was packaged in Al foil to protect the rare-earth Ce from oxidation. The alloys were melted using a vacuum furnace under an argon atmosphere. The ingots were then melted at 1200 °C for 2 min. The mixture was melted and then cooled down naturally. The size of sample was 20 mm in diameter and 45 mm in height.

![Figure 1. Phase diagram of Al-Bi alloys [16].](image)
Al-20% Bi ingots were sectioned longitudinally and prepared by standard grinding procedures. They were finally polished with colloidal silica suspension to observe the microstructure. In order to detect the compound, XRD was performed by using a Cu Kα source. X-ray diffraction was measured on an X’Pert Pro type tester. The morphology of specimens was examined using a SS-550 scanning electron microscope equipped with an energy dispersive X-ray spectrometer (EDS). The microstructures were analyzed by SEM to characterize the distribution of the entire phase of alloys. The sample was chosen and analyzed from top to bottom (as shown in Figure 2) in order to characterize the distribution of the entire primary phase.

![Sample Microstructure](image)

**Figure 2.** The sample chosen for analysis of the microstructure.

### 3. Results and Discussion

#### 3.1. Effect of Rare-Earth Ce on the Alloy Microstructure

The SEM images of Al-Bi immiscible alloys with and without 2 mass% Ce are shown in Figure 3. It shows the effect of Ce additive on the liquid phase segregation of Al-Bi immiscible alloys. The ingot height is 40 mm. Measurement points 10 mm, 20 mm, and 30 mm from the bottom of the ingot were analyzed. The black phase is Al-rich matrix and the white phase is Bi-rich droplets by EDS analysis. During solidification, the alloys melt-separate into an Al-rich zone and Bi-rich droplets, as shown in Figure 3a. Large droplets are found in Al-Bi alloys without Ce, and the distribution of droplets is non-uniform. The large Bi droplets mainly exist in the bottom of the sample, indicating a considerable gravity segregation. The mean diameter of Bi-rich droplets is approximately 42 μm. The microstructure of Al-Bi immiscible alloys is similar to those seen previously in the literature [13]. The size of Bi-rich droplets increases gradually from top to bottom, which is a typical microstructure of immiscible alloys. During cooling, the Bi-rich phase nucleates and grows by diffusion to form large droplets, which tend to coalesce and segregate.

The longitudinal microstructure of Al-Bi alloy with Ce is different from that without Ce, as shown in Figure 3b. The size and distribution of Bi-rich droplets are refined when rare-earth Ce is added. It can be seen that the Bi-rich droplets are more homogeneously distributed throughout the Al matrix, as compared with the microstructure of binary Al-Bi alloys without the addition of Ce. The average diameter of Bi-rich droplets is approximately less than 5 μm. The distribution of Bi-rich droplets from top to bottom along the direction of gravity was analyzed. The images show that the droplets are also distributed uniformly along the direction of gravity.

The size distribution of Bi-rich droplets in Al-Bi alloys with and without Ce are plotted and shown in Figure 4. The statistics of the diameters of Bi-rich droplets is counted in the longitudinal section. Without the addition of Ce, the size distribution is broader, and there are fewer droplets. With the addition of Ce, the distribution of Bi droplets becomes narrower, and the diameters of the wide-spread distribution of droplets are less than 5 μm. The plots show that the addition of Ce led to a decrease in the range of distribution. The comparison result indicates that the addition of rare-earth Ce was efficient in achieving a dispersed distribution of Bi-rich droplets.
When the content of Ce is less, there is insufficient compound to act as heterogeneous sites. The content Ce, the average diameter of Bi-rich droplets continues to decrease in size. Few rod-like CeBi droplets is about 20 μm. The content of rare-earth Ce increases from 1 mass% to 2 mass%, and then to 4 mass%. With increasing Ce content, the microstructure is not clearly refined. Without less than 1 mass% Ce, the microstructure is not clearly refined.

Figure 3. SEM microstructure of Al-20Bi alloys. Without Ce, (a) 30 mm, (c) 20 mm, and (e) 10 mm from the bottom; and with 2 mass% Ce, (b) 30 mm, (d) 20 mm, and (f) 10 mm from the bottom.

Figure 4. Size distribution of Bi-rich droplets in Al-Bi alloys (a) without Ce, and (b) with 2% Ce.

3.2. Effect of Rare-Earth Ce Content on the Alloy Microstructure

From the phase diagram in Figure 5, the intermetallic compound has been identified as CeBi₂, corresponding to the EDS point analysis. Nucleation of Bi-rich droplets is stimulated by precipitated CeBi₂. Then, additional Bi liquid phase nucleates around the intermetallic CeBi₂, growing rapidly to obtain a dispersed microstructure. This refinement is attributed to intermetallic CeBi₂ compounds that are dispersively distributed in the matrix and promote the heterogeneous nucleation.

Figure 6 shows that the solidified microstructures of Al-Bi-Ce alloys vary with the additive content of rare-earth Ce. With the addition of less than 1 mass% Ce, the microstructure is not clearly refined. When the content of Ce is less, there is insufficient compound to act as heterogeneous sites. The content of rare-earth Ce increases from 1 mass% to 2 mass%, and then to 4 mass%. With increasing Ce content, the diameter of Bi-rich droplets decreased. With 1 mass% Ce addition, the average diameter of Bi-rich droplets is about 20 μm. It can be seen from Figure 6a that the CeBi₂ phase is covered with Bi-rich droplets. However, Bi-rich droplets still appear as large diameter. With further addition of 2 mass% Ce, the average diameter of Bi-rich droplets continues to decrease in size. Few rod-like CeBi₂ phases...
(that are not covered) are presented in Figure 6b. Until the content of Ce is 4 mass%, a large number of long CeBi$_2$ rods are found in the Al matrix in Figure 6c. With a further increase in the content of rare-earth Ce, the size of the intermetallic compound CeBi$_2$ increases, and the Bi-rich phase decreases due to the reaction between Bi and Ce.

Figure 5. Phase diagram of Bi-Ce alloys [24].

Figure 6. Solidified microstructures of Al-Bi with different additive amount of Ce: (a) 1%, (b) 2%, (c) 4%.
The content of rare-earth Ce affected the amount of intermetallic CeBi₂. Meanwhile, the intermetallic compounds affected the second phase segregation. The size and dispersal of Bi-rich droplets would effectively increase the self-lubricating performance. Therefore, controlling the size and number of the second phase is important in order to obtain uniform dispersive microstructure. The addition of rare-earth Ce at 2 mass% has shown positive results, as Bi-rich droplets refined and decreased in size.

3.3. Al-Bi-Ce in Situ Compound

X-ray diffraction analyses are performed to determine the phase constitution of Al-Bi-Ce alloys, shown in Figure 7. The multiple diffraction peaks correspond to the reflection for Al-Bi phases. The contents of Al and Bi in the composite with Ce are almost the same as that without Ce, which indicates that the matrix and the second phases are not changed when the rare-earth Ce is added. No other intermetallic phase was detected from X-ray diffraction. No intermetallic compound diffraction peaks were detected—it may be covered by the broad diffraction peaks of Al and Bi.

![Figure 7. XRD patterns of Al-Bi-2% Ce alloy.](image)

The microstructure of the Al-Bi-2 mass% Ce alloy is shown in Figure 8a. It can be seen that in each Bi-rich droplet there is a rod-like intermetallic compound. Figure 8b shows the EDS point analysis of the rod included into the droplet. It demonstrates that the intermetallic compound is CeBi₂ due to atomic ratio, corresponding to the phase diagram and shows that no other phases are found in the image. CeBi₂ is the only reaction product between Bi and Ce elements. It should be noted that the CeBi₂ intermetallic compounds are all observed inside Bi-rich droplets, which is presented one or two rods. The results are carried out to identify the existence of intermetallic CeBi₂ by detecting each Bi-rich droplet. It is expected that the surface of dispersively suspending CeBi₂ in a solidifying melt would be a site for heterogeneous nucleation. It can be seen that the wetting angle is less than 90°, as shown in Figure 11. There is clear evidence that Bi phases are able to wet the CeBi₂ particle. Figure 8 shows the existence of Bi-rich droplets nucleated on the CeBi₂ surface.

![Figure 8. SEM image of (a) Bi-rich droplets, and (b) EDX point analysis of rod-like compounds.](image)
The EDS mapping analysis verifies that Bi-rich droplets consist of Bi and Ce phases. As can be seen in Figure 9, different color points, respectively, represent Al, Bi, and Ce, and that each component is distributed evenly. Rare-earth Ce is clearly shown to be dispersed in the Bi-rich droplets, mainly focused in the CeBi₂ rods. The intermetallic CeBi₂ located inside the Bi-rich droplets is to be used as inoculants for heterogeneous nucleation.

![Figure 9. The corresponding EDS mapping analysis of Bi-rich droplet.](image)

The addition of rare-earth Ce only formed an intermetallic compound with Bi, without chemical reaction in the Al matrix. The Bi-rich minority droplets nucleate dispersively because the amount of rods is large. The in situ intermetallic compounds act as heterogeneous inoculants and have influence mainly on the coalescence and segregation of Bi-rich droplets, without influence on the performance of Al-Bi alloys.

There is evidence that Bi-rich droplets nucleate on the precipitated CeBi₂ surface; therefore, CeBi₂ acted as nucleation centers. Then, Bi liquid phase continued to grow on the intermetallic CeBi₂, and the large amount of CeBi₂ rods led to a dispersive microstructure. Rare-earth Ce increases the number of Bi-rich droplets and decreases the size of droplets. Hence, the refinement of Bi-rich droplets by the addition of Ce is attributed to intermetallic CeBi₂.

### 3.4. Contact Angle of CeBi₂

The addition of rare-earth Ce effectively suppresses the liquid–liquid macrosegregation of Al-Bi immiscible alloys. The in situ intermetallic compounds can serve as inoculants to obtain a uniformly-dispersed microstructure. Inoculants lead to a high number of Bi-rich droplets and reduce the size of Bi-rich droplets. The smaller Bi-rich droplets are thereby less-susceptible to Stokes motion, Marangoni convection, and coagulation. The nucleation of Bi-rich droplets on intermetallic compounds can be described by the heterogeneous nucleation theory for melts with an intermetallic phase. The heterogeneous nucleation process is mainly controlled by the interfacial free energy at the nucleating interface. It can be calculated by:

\[
\cos\theta = \frac{\sigma_{SL1} - \sigma_{SL2}}{\sigma_{L1L2}}
\]
where $\theta$ is the contact angle, $\sigma_{L_1L_2}$ is the interfacial energy between phases $L_1$ and $L_2$, $\sigma_{SL_1}$ is the interfacial energy between the $L_1$ phase and the nucleation substrate, and $\sigma_{SL_2}$ is the interfacial energy between the $L_2$ phase and the nucleation substrate. However, the equation is not the real equilibrium relation. The nucleation sites cause the variation of Gibbs free energy.

$$
\Delta G_{\text{het}} = \left( \frac{4}{3} \pi r^3 \Delta \tilde{G}_1 + 4 \pi r^2 \sigma_{L_1L_2} \right) \left( \frac{2 - 3 \cos \theta + \cos^3 \theta}{3} \right) = \Delta G_{\text{hom}} f(\theta)
$$

where $\Delta G_{\text{het}}$ is the Gibbs free energy of heterogeneous nucleation, $\Delta G_{\text{hom}}$ is the Gibbs free energy of homogeneous nucleation, and $\Delta \tilde{G}_1$ is the Gibbs free energy of the nucleation site.

Cai et al. [25] indicated that the addition of SiC particles reinforced magnesium composite. The heterogeneous nucleation on SiC particles occurred because the eutectic and Cu$_2$Zn$_8$ phases are able to wet the SiC particles. It is indicated that the contact angle directly determines the degree of difficulty of heterogeneous nucleation. The inoculants must be preferably wetted by liquid $L_2$ in the presence of liquid $L_1$, as shown in Figure 10. However, it is difficult to measure the contact angle. In order to see the contact angle, the ratio of rare-earth Ce is increased to 4 mass%, as shown in Figure 11. It is clearly seen from the SEM images in Figure 11 that the CeBi$_2$ compounds are wetted by the Bi phase. The average contact angle is approximately 18°, by measurement in the images. The smaller the contact angle, the smaller the free energy of heterogeneous nucleation [26]. So, it is believed to promote the nucleation of the Bi-rich phase due to the smaller contact angle. Hence, the experimental results demonstrate that the addition of rare-earth Ce can restrain liquid phase segregation for the heterogeneous routes.

![Figure 10. Definition of the contact angle.](image)

![Figure 11. Solidified microstructures of Al-Bi with 4% Ce.](image)

### 4. Conclusions

In summary, Al-Bi immiscible alloys are effectively fabricated with dispersed fine second phase droplets by the addition of rare-earth Ce. It is shown that Ce induces a reduction in the size of Bi-rich droplets in binary Al-Bi immiscible alloys, and increases the number of droplets. The Bi-rich droplets of the ternary Al-Bi-Ce alloys are more homogeneously distributed throughout the Al-matrix, as compared with the microstructure of binary Al-Bi alloys without rare-earth Ce. The effect of Ce addition on the Bi-rich phase is due to the intermetallic rod-like CeBi$_2$ compounds produced during
solidification. The Bi phase nucleates on the CeBi$_2$ compound’s surface. This suggests that the CeBi$_2$ compound served as inoculant, resulting in heterogeneous nucleation on them. When the content of rare-earth Ce achieves 2 mass%, the number of fine CeBi$_2$ rods is enough to act as inoculant to obtain the optimal microstructure. There is much more dispersive minority of Bi-rich droplets within the Al matrix due to heterogeneous nucleation. The experimental results indicate that gravity segregation can be suppressed by the addition of Ce.

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References


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