In situ synchrotron study of liquid phase separation process in Al-10 wt.% Bi immiscible alloys by radiography and small angle X-ray scattering

W Q Lu\textsuperscript{a}, S G Zhang\textsuperscript{b} and J G Li\textsuperscript{c}

School of Materials Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Rd., Shanghai 200240, China

E-mail: \textsuperscript{a}flytsing1003@sjtu.edu.cn, \textsuperscript{b}sgzhang@sjtu.edu.cn, \textsuperscript{c}lijg@sjtu.edu.cn

Abstract. Liquid phase separation process of immiscible alloys has been repeatedly tuned to create special structure for developing materials with unique properties. However, the fundamental understanding of the liquid phase separation process is still under debate due to the characteristics of immiscible alloys in opacity and high temperature environment of alloy melt. Here, the liquid phase separation process in solidifying Al-Bi immiscible alloys was investigated by synchrotron radiography and small angle X-ray scattering. We provide the first direct evidence of surface segregation prior to liquid decomposition and present that the time dependence on the number of Bi droplets follows Logistic curve. The liquid decomposition results from a nucleation and growth process rather than spinodal decomposition mechanism because of the positive deviation from Porod’s law. We also found that the nanometer-sized Bi-rich droplets in Al matrix melt present mass fractal characteristics.

1. Introduction

Aluminium-based immiscible alloys have shown promising applications on bearing if a unique microstructure consisting of homogenous dispersed soft phase within an Al matrix is obtained [1]. However, liquid decomposition occurs mainly due to the density difference between two liquid and temperature gradient because of the Marangoni motion in solidifying immiscible alloys. Many studies have been carried out to further study the liquid phase separation process (LPSP) [2-8]. It was shown that it occurs as the formation of minor droplets by the spinodal decomposition [3, 5] or the nucleation and growth mechanism [9-11]. However, as the LPSP either occurs at high temperature or is hidden by solidification, it is the major obstacle and challenge for the experimental investigation.

Recently, synchrotron radiography experiments have been performed to investigate the LPSP of the Al-Bi immiscible alloys [2, 3, 12]. Schaffer et al. [2, 3] reported that the interaction between the Bi droplets and solidification front is decisive for final solidification structure. Wang et al. [12] found that the Bi droplets seriously aggregated with the presentation of the electric current pulse. However, they did not show the changes in Bi droplets number with time during the LPSP, and they also did not discuss the exact mechanisms of the LPSP.

Small angle X-ray scattering (SAXS) has always been used to determine whether a phase transformation results from spinodal decomposition mechanism or nucleation and growth process [13-15]. It is also a powerful means to investigate the liquid structure in nanometer scale [16]. According to the Al-Bi phase diagram, the mole fraction of Bi in the Bi-rich minor droplets changes with temperature during the LPSP [17]. Thus, the structure of the Bi-rich minor droplets is different
at different temperatures. However, there is no experimental investigation in the LPSP by SAXS. Here, besides direct imaging of the behaviour of the Bi-rich droplets and its effect on the morphology evolution in solidifying Al-10 wt.% Bi immiscible alloy, *in situ* synchrotron SAXS technique is used to investigate the structure of the Bi-rich minor droplets in nanometer scale.

2. Experimental procedures

The Al-10 wt.% Bi alloy spheres were prepared from pure Al(99.99%) and pure Bi(99.99%) by one-step fabrication method, the detailed preparation process can be found elsewhere [18]. The imaging and SAXS experiments were carried out at beam lines BL13W1 and BL16B1 of Shanghai Synchrotron Radiation Facility (SSRF), respectively. Figure 1 shows the sketch of the experimental device configuration at SSRF. An alloy sphere was placed on a Cu sheet for imaging or a MgO sheet for SAXS experiment in furnace body, the furnace body was evacuated to $10^{-4}$ Pa and backfilled argon to 0.1 MPa. The sample was heated and cooled by a 100 W CO$_2$ laser with the focused beam hitting the specimen from the top. The temperature was measured by infrared pyrometer. The imaging and SAXS experiments were carried out at the same cooling rate. However, in order to guarantee the uniformity and stability of the melts temperature, the specimen used in SAXS experiment was placed on the MgO Sheet.

At imaging beam line station, the energy of the synchrotron X-ray beam was 30 keV. The exposure time per frame was 1 s. The effective pixel size was limited to 0.74 μm. Image Pro Plus 6.0 image analyzer software was used to measure the number of the Bi-rich minor droplets.

At SAXS beam line station, the energy and wavelength of the incident beam are 17 keV and 0.73 Å, respectively. The distance between specimen and CCD detector was 5.396 m. A Mar CCD 165 detector was used to record the scattered X-ray. The range of scattering vector (q) and scattering angle ($2\theta$) are 0.086~0.637 nm$^{-1}$ and 0.058~0.424°, respectively. The scattering intensities were obtained from 2-D SAXS pattern after background subtracting by Fit-2D software.

![Figure 1. The schematic of experimental device configuration at SSRF.](image)

3. Results and discussions

3.1 Segregation morphology evolution and larger sized droplets behaviour

Figure 2 shows the segregation evolution in solidifying Al-10 wt.% Bi immiscible alloy. The light grey phase is Al-rich phase, while the dark phase is Bi-rich phase because of the different absorption coefficient of X-ray between Al and Bi. The bright region in the bottom of the alloy melt is a hydrogen
bubble which nucleates on the Cu sheet and increases its size with time (figure 2a). From figure 2b, Bi-rich droplets appear in the bubble area prior to other parts of the alloy melt.

There is a temperature gradient across the alloy sphere from bottom up because the sample was placed on a Cu sheet and heated by a CO$_2$ laser from the top. Furthermore, the energy change is about $-1.4 \text{ ev}$ for exchanging a Bi atom in the bulk with an Al atom on the surface [19]. Thus, Bi atom approaches to bottom and surface to decrease the system free energy (figure 2b). The amount of the precipitation Bi-rich phase increases with decreasing temperature (figure 2b-c). After surface segregation, some Bi-rich droplets separate out from matrix melt outside of the bubble area, meaning that bulk phase separation occurred. This experiment directly confirms that surface segregation takes place before the LPSP, yielding consistent results with the numerical simulations [20].

![Figure 2](image)

**Figure 2.** The morphology evolution during the solidification of the Al-10 wt.% Bi immiscible alloy with the cooling rate of 1.6 K/s. The temperature of the sample at time zero is 1417 K.

Once the Bi-rich droplets nucleated, they were instantaneously exposed to a force field [3, 21]. Besides Marangoni motions [1], they were also acted on by the Stokes motion [3]. As seen in figure 2, the position of the Bi-rich droplets did not change because the Marangoni motion can’t overcome the Stokes motion.

From figure 2, the number of Bi-rich droplets inside the bubble area is unchanged after 210.78 s. However, the number of Bi droplets number of the bubble area changes with the extension of time. Figure 3 shows the change in Bi droplets number over time during LPSP. It can be seen that, the droplets number increases with time at the initial stage of the LPSP, while it reaches a constant value at the later stage. On cooling a homogenous melt of Al-Bi immiscible alloy, the continuous decrease of temperature increases the supersaturation of Bi atoms in Al matrix [22]. Its increase leads to a rapid increase of the nucleation rate, thus the droplets number increase rapidly. Meanwhile, as the surface segregation and the formation of Bi-rich droplets consume a large amount of Bi atoms in Al matrix, the size of newly formed Bi-rich droplets decreases (figure 2e-f). At the final stage of the LPSP, the Bi solute is almost all deposited from the Al matrix melt, leading to saturation of the number of the Bi-rich droplets. Therefore, characterized by a saturation level characteristic [23], the Logistic population model should be applied satisfactorily to the change of the number of Bi-rich droplets during the liquid phase separation period, and it can be described as:

$$ N = 300.3 + \frac{32 \cdot 300.3}{1+\left(\frac{t}{293.7}\right)^{76.7}} \quad (1) $$

3
3.2 Occurrence mechanism of the liquid phase separation

The relative scattering intensity curves $I(q)$ vs. $q$ as a function of temperature obtained from Al-10 wt.% Bi immiscible alloy are presented in figure 4a. It can be seen that the scattering intensity significantly increases at 863 K due to crystallization. The scattering intensities are different at low $q$ region but reach a constant value at high $q$ region.

Figure 4. (a) $I(q)$ vs. $q$ as a function of temperature obtained from Al-10 wt.% Bi immiscible alloy with the cooling rate is 1.2 K/s, the error limit of measure temperature is ±2.4 K. (b) $\ln[q^3I(q)]$ vs. $q^2$ at different temperatures, the positive deviation from Porod’s law was corrected.

3.2.1 As an ideal two phase system has a certain constant electron density difference and sharp boundary, the scattering intensity plot obeys Porod’s law, i.e. $\lim_{q \to \infty} q^2I(q) = K'$, where $K'$ is the Porod constant [24]. However, there is positive or negative deviation from Porod’s law for a non-ideal system when electron density fluctuation or a diffuse interface layer exists in any phase [16]. Therefore, Porod’s law can be adopted to determine whether the LPSP of Al-Bi immiscible alloys results from a nucleation and growth process or spinodal decomposition mechanism. Figure 4b shows the plot of $\ln[q^3I(q)]$ vs. $q^2$ calculated from figure 4a during the LPSP of Al-10 wt.% Bi immiscible alloy. It can be seen that there is a positive deviation from Porod’s law. According to Li et al. [16] and Li [25], this positive deviation means that the electron density changes abruptly in the Al-matrix melt and there is a sharp boundary rather than a diffuse interface layer between Bi-rich droplets and Al-matrix melt. So we
think that the LPSP occurs as the nucleation of Bi-rich droplets directly from the supersaturated Al-matrix melt rather than a homogeneous spinodal reaction.

From figure 4b, the plot of $\ln[q^3 I(q)]$ vs. $q^2$ was fitted by $\ln[q^3 I(q)]=\ln K'+\sigma^2 q^2$ at high $q$ region. Suggested by Li [26], the positive deviation was corrected to calculate $K'$. And the width ($L$) of electron density fluctuation can be calculated by $L=\sqrt{2\pi \sigma}$ with $\sigma^2$ representing the slope of the ln $[q^3 I(q)]$ vs. $q^2$ at high $q$ region [27]. Based on the above equations, $L=4.86$ nm, which was independent of the temperature, yielding consistent results with the electron density fluctuation in Al-15 wt.% Cu melt [16].

3.3 Liquid structure of the nanometer-sized droplets

The size of the scattering objects (here is the Bi-rich minor droplets) can be analyzed by the Guinier approximation, which can be described by

$$ I(q) \propto \exp\left[-\left(R_G q\right)^2/3 \right] $$

with $R_G$ representing gyration radius. $R_G$ can be calculated by $R_G = (3k)^{1/2}$ with $k$ is the initial slope of the plot ($\ln I(q)$ vs. $q^2$) [16, 28]. For spherical particle, $R_s = \frac{\pi}{5} R$ [29]. Therefore, the radius of the newly formed Bi-rich droplets is about 14.2 nm. According to the phase diagram of Al-Bi immiscible alloy [17], the temperature dependence of the mole fraction of Bi in the Bi-rich droplets can be described as [28]:

$$ C(Bi) = -0.1737 + (2.71\times10^{-3} -1.74\times10^{-6}T)T $$

(2)

From the equation (2), the relationship between the mole fraction of Bi in the Bi-rich droplets and temperature is plotted in figure 5. It can be seen that the mole fraction of Bi in the Bi-rich droplets increases with decreasing temperature during the liquid decomposition period. Thus, the liquid structure of the Bi-rich droplets under different temperature is different. Similar to the clusters of metallic melts [29], the nanometer-sized Bi-rich droplets can present fractal characteristic. The scattering intensity on a fractal structure is often described by $I(q) \propto q^{-\alpha}$, where $\alpha$ is related to fractal dimension and it can be calculated by the slope ($-\alpha$) of $\ln I(q)$ vs. $\ln (q)$. For mass dimension, $D_m=\alpha +1$ [16].

Figure 6 shows the changes of fractal dimension with the temperature during liquid phase separation stage. It can be seen that the maximum value of the fractal dimension appears at 934 K close to the monotectic transition temperature. This means that the newly formed Bi-rich droplets at 934 K are most compact. Suggested by Sonntag and Russel [30], if the fractal dimension of the aggregate is about 2.48, its structure is 3D flocs. As the dimensions of the Bi-rich droplets is in the range of 2.39~2.56, the newly formed Bi-rich droplets during liquid phase system. Thus, the fractal dimension of the Bi-rich droplets is different from the diffusion limited cluster aggregation (DLCA) model [31]. Therefore, the Bi-rich droplets formed by nucleation and growth have compact structure during the initial stage of growth.
Figure 6. $\ln[I(q)]$ vs. $\ln(q)$ as a function of temperature separation process are 3D flocs. It should be noted that the nature of metallic melts is significantly different from the flocculation of colloidal.

4. Summary
Synchrotron radiography and small angle X-ray scattering have been used to investigate the LPSP of the Al-Bi immiscible alloys. We found that the LPSP occurs by the nucleation of Bi-rich droplets, which present mass fractal characteristics. We also found that the time dependence on the number of Bi droplets follows Logistic curve and provide the first experimental evidence that surface segregation occurs before liquid decomposition.

Acknowledgments
We thank the staff members of the BL13W1 and BL16B1 beam lines of SSRF and Z.Y. Dai for helping to prepare for the synchrotron experiments. This work is supported by the National Natural Science Foundation of China (Nos. 51027005 and 51271119), the Shanghai Science & Technology Committee (No. 11JC1405900).

References
[1] Ratke L and Diefenbach S 1995 Mater. Sci. Eng. R 15 263
[2] Schaffer P L, Mathiesen R H and Arnberg L 2009 Acta Mater. 57 2887
[3] Schaffer P L, Mathiesen R H, Arnberg L, Sabatino M D and Snigirev A 2008 New J. Phys. 10 1
[4] Wang W L, Li Z Q and Wei B 2011 Acta Mater. 59 5482
[5] Wang C P, Liu X J, Ohnuma I, Kainuma R and Ishida K 2002 Science 297 990
[6] Shi R P, Wang C P, Wheeler D, Liu X J and Wang Y 2013 Acta Mater. 61 1229
[7] Luo B C, Liu X R and Wei B 2009 J. Appl. Phys. 106 053523
[8] Ratke L 1995 Mater. Sci. Eng. A 203 399
[9] Wu M, Ludwig A and Ratke L 2003 Metall. Mater. Trans. A 34 3009
[10] Tegze G, Pusztai T and Granasy L 2005 Mater. Sci. Eng. A 413-414 418
[11] Wu M H, Ludwig A, and Ratke L 2003 Simul. Mater. Sci. Eng. 11 755
[12] Zhu J, Wang T M, Cao F, Fu H W, Fu Y N, Xie H L and Xiao T Q 2013 J. Mater. Eng. Perform. 22 1319
[13] Chai Z G and Meng C F 1998 J. Appl. Cryst. 31 7
[14] Meng F L, Chai Z G and Wang Y M 2000 J. Mater. Sci. Lett. 19 1837
[15] Wu Z D, Lu X H, Wu Z H, Kui H W 2014 J. Non-Cryst. Solids 385 40
[16] Li F G, Zhang J, Dai Y B, Bian F G, Han Y F, Sun B D 2014 Mater. Chem. Phys. 143 471
[17] 1986 Binary Alloy Phase Diagrams vol 1, ed T B Massalski (Ohio: American Society of Metals)
[18] Dai R, Zhang S G, Li Y B, Guo X and Li J G 2011 J. Alloys Compd. 509, 2289
[19] Zhang X M, Liu J C, Tang J G, Li L, Chen M G, Liu S D, Zhu B 2010 Appl. Surf. Sci. 256 7300
[20] Qin T, Wang H P and Wei B 2007 Sci. Chin. G 37 409
[21] Lu W Q, Zhang S G and Li J G 2013 Mater. Lett. 107 340
[22] Guo J J, Liu Y, Jia J, Su Y Q, Ding H S, Zhao J Z and Xu X 2001 Scr. Mater. 45 1197
[23] Wu H, Chakraborty A, Li BL and Kenerley C M 2009 Ecol. Complex. 6 403
[24] Porod G 1951 Kolloid-Z 124 83
[25] Li Z H 2013 Chin. Phys. C 37 108002
[26] Li Z H, Zhao J P, Wu D, Sun Y H, Wang J, Liu Y, Sheng W J and Dong B Z 2000 Acta Chim. Sin. 58 1147
[27] Hashimoto T, Fujimura M and Kawai H 1980 Macromolecules 13 1237
[28] Zhao J Z, Li H L, Li H Q, Xing C Y, Zhang X F, Wang Q L and He J 2010 Comput. Mater. Sci. 49 121
[29] Ding G H, Zu F Q, Li X F, Xi Y and Shen R R 2006 Acta Phys. Sin. 55 4188
[30] Sonntag R C and Russel W B 1987 J. Colloid Interface Sci. 115 378
[31] Liu J, Shih W Y, Sarykaya M and Aksay I A 1990 Phys. Rev. A 41 3206