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Cu segregation on the heterogeneous nucleation interface between Al₂O₃ substrate and Al-1.4Cu alloy

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Abstract

Composition and structure at the heterogeneous nucleation interface has an important effect on the potency of heterogeneous nucleation. Here, we used HAADF-STEM imaging and quantitative EDX analysis to elucidate the Cu segregation at the heterogeneous nucleation interface between Al₂O₃ substrate and Al-1.4Cu alloy. A significant Cu segregation (about 2 at %) was observed, which can be attributed to

twofold: the enhanced diffusion caused by the high strain with large lattice misfits (9.45 %) and the chemical reaction between Al_2O_3 substrate and Al-1.4Cu alloy. This investigation highlights the importance of Cu segregation on the heterogeneous nucleation of Al on Al_2O_3 substrate.

Keywords: Al alloys; Segregation; Al_2O_3 substrate; High-angle annular dark field (HAADF); Energy-dispersive X-ray spectroscopy (EDX).

Grain refinement of Al alloy is of great necessity to improve casting quality, in particular to the hot tearing of Al-Cu based alloys. Adding effective nucleating substrates (i.e. TiB_2) to the liquid Al for inoculation is generally believed to be one of most efficient ways to achieve an enhanced grain refinement of Al alloy [1, 2]. However, the potency of heterogeneous nucleation can be affected by many factors, including the size and size distribution of the nucleating substrates as well as the interface composition and structure [1-4]. A typical example is that the formation of Al_3Ti phase on the basal plane of TiB_2 is believed to reduce the lattice mismatch, lower the nucleation barrier and thereby enhance the heterogeneous nucleation, even with the same growth restriction factor and the same amount and type of TiB_2 addition [3, 4]. This strongly indicates that tailoring the interface composition and structure is a key point to improve the potency of heterogeneous nucleation and thereby grain refinement.

Many models (i.e. adsorption model [5, 6], free growth model [3, 4]) have been proposed to interpret the presence of the initial layer (i.e. Al_3Ti phase) on the nucleating particle surface (i.e. TiB_2). However, it should be noted here that the adsorption on the nucleating particle surface can be affected by many factors: i.e. the roughness of the substrate, the segregation of other alloying element, the orientation relationship and lattice mismatch between substrate and nucleus [7-9]. A systematic investigation on these factors is required. However, in conventional solidification and / or casting process, such type of investigations seems to be impossible because of the fact that the presence of impurities (i.e. Fe) is unavoidable and the adjustment of the orientation relationship and lattice mismatch is impossible. More importantly, due to the fact that only very few nucleating particle (i.e. less than 5 %) can be activated for the heterogeneous nucleation and the

activated nucleating particle is very likely to be destroyed or lost during the sample preparation process for further high resolution characterisation, the investigation on the interface composition and structure becomes very time-consuming and high-costs. One possible alternative way is to employ melt spinning to freeze the nucleating particle into the metal glass matrix and then characterise the composition and structure of heterogeneous nucleation interface [10]. A typical example is that the crystallization of amorphous Al alloy on TiB_2 substrates has been investigated in order to demonstrate the heterogeneous nucleation of Al alloy [10]. A layer of Al_3Ti at Al/ TiB_2 interface was observed [10]. To date, it was well accepted that the formation of Al_3Ti layer is responsible for the enhanced heterogeneous nucleation of Al on TiB_2 . However, the nucleation behaviour under rapid solidification condition may be different from that under conventional solidification condition. Especially, the diffusion of alloying elements under rapid solidification condition is much lower than that under conventional solidification condition.

In order to perform such type of systematic investigations, an experimental setup under controlled nucleation process by solidifying a high purity Al droplet on a single crystal substrate in a high vacuum chamber has been built to elucidate the heterogeneous nucleation, with a special focus on the wetting angle and undercooling measurement [7, 11, 12]. However, it should be noted here that, due to the lack of TiB_2 single crystal in the commercial market, such type of systematic investigations has been mainly performed in Al / $\alpha\text{-Al}_2\text{O}_3$ system because it has exhibited large nucleation undercooling (175 °C) [7]. For example, the ordering of liquid Al atoms (rather than being a pure Al layer) in the vicinity of the heterogeneous nucleation interface by knocking oxygen atoms out of

α -Al₂O₃ wafer has been reported [13, 14]. Furthermore, the ordering degree of the layer which varies as a function of adjacent crystal planes has been investigated [15]. However, whether the heterogeneous nucleation starts from the ordering structure still remains to be explored. Furthermore, adding ternary alloying element (i.e. Sb) into liquid Al also affects the formation of the epitaxial layer of Al [11]. On the other hand, a chemical reaction between liquid and substrate has also been reported [11, 16, 17]. The nucleation of Al on the MgO substrates was actually nucleated on MgAl₂O₄ by the chemical reaction of Al and MgO [11]. Although Cu is one of the most important alloying elements in Al alloys, there is still a lack of a detailed investigation on the effect of the Cu addition into liquid Al on the formation of heterogeneous nucleation interface of α -Al₂O₃ substrate.

In this paper, HAADF-STEM imaging and quantitative EDX analysis was used to elucidate the Cu segregation at the interface between Al₂O₃ substrate and Al-1.4Cu alloy. The effect of Cu segregation on the potency of heterogeneous nucleation is also discussed.

The substrate with (10-10) crystal planes was cut from one single crystal α -Al₂O₃. The surface roughness of the substrates is less than 5 nm. The substrates were ultrasonic cleaned in acetone solution prior to experiment. High purity Al (99.999 wt %) was purified using glass fluxing method to remove potential heterogeneous nuclei from liquid Al. The lattice misfit ((100)Al / (10-10)) is calculated to be 9.45 % according to Bramfitt equation [7, 18]. In order to examine the effects of Cu solute on the interfacial structure tuning, high purity Cu (99.999 wt %) was added by Al-Cu master alloy into liquid Al with a concentration of 1.4 wt % after purification. It should be noted that the concentration (1.4 wt %) was selected for a prior precipitation order of Al-Cu solid solution according

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to Al-Cu phase diagram. Al-Cu mater alloy was prepared by arc melting under an argon atmosphere, and then directly casted into cylindrical rods with 3 mm diameter using a suction casting facility. It should be noted here that impurities may be present during the arc melting process.

The TEM sample was prepared from cut slices perpendicular to the interface and then mechanically ground, polished and dimpled to about 30 μm in thickness, ion-beam milled using a Gatan Precision Ion Polishing System (PIPS, Gatan model 691). A preparation temperature (about -10 $^{\circ}\text{C}$) was kept constant by using a cold stage during ion beam polishing. Conventional TEM investigation was performed using a Philips CM12 microscope operated at 120 kV equipped with a CCD-camera (GATAN Model 794 MSC BioScan). An FEI Titan G2 80–200 ChemiSTEM™ (S)TEM fitted with an X-FEG high brightness electron source and a Super-X 4 SDD EDX detector system with an elevation angle of $\sim 18^{\circ}$ was employed to measure the Cu segregation on the substrate (Al_2O_3). Spectrum imaging was performed using an accelerating voltage of 200 kV, a convergence semi-angle of 21 mrad and a beam current of 1.2 nA, providing count rates of >50,000 counts/second which enabled pixel-by-pixel semi-quantitative compositional mapping. HAADF imaging in the Titan was performed with a HAADF inner angle of 60 mrad.

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Figure 1 shows bright field TEM micrographs (Figure 1a, c) and corresponding selected area electron diffraction (SAED) (Figure 1b, d) across the interface between Al_2O_3 substrate and Al-1.4Cu alloy. It should be noted here that, in Figure 1a, b, Al_2O_3 substrate was tilted to [011] zone axis, while, in Figure 1c, d, Al matrix was tilted to [011] zone axis. The tilting angle is about 20 $^{\circ}$. Clearly, there is no orientation relationship between

Al₂O₃ substrate and Al matrix. Further detailed observation shows that the interface is not flat and smooth. Instead, a zigzag morphology was observed, as shown in Figure S1. This can be attributed to twofold: the roughness of the Al₂O₃ substrate and the chemical reaction between Al₂O₃ substrate and Al-1.4Cu alloy, which is consistent with the formation of MgAl₂O₄ in the Al and MgO system. Indeed, intermetallic phase (i.e. Al₂Cu) appears to be present at the interface, as shown in Figure S1. Dislocation with a high number density was also observed within the Al matrix in the vicinity of the interface, as shown in Figure S2, which can be attributed to the high strain caused by the large lattice misfits (9.45 %). The presence of the dislocation may enhance the diffusion of Cu at the interface, as shown in Figures 2-4.

Figure 2 shows HAADF-STEM micrograph (Figure 2a) and EDX elemental maps of Al (Figure 2b), Cu (Figure 2c), O (Figure 2d), Ti (Figure 2e), Fe (Figure 2f) across the interface between Al₂O₃ substrate and Al-1.4Cu alloy. In this low magnification, no significant Cu segregation at the interface was observed. However, Cu-rich phase (very likely to be Al₂Cu phase formed during the solidification) was observed within the Al matrix, as shown in Figure 2c. Furthermore, it should be noted here that a very trace of Ti was also observed, which can be attributed to the impurities induced during the sample melting process (arc melting). However, the presence of trace Ti is not believed to play a significant effect on the nucleation of Al on the Al₂O₃ substrate.

Figure 3 shows HAADF-STEM micrograph (Figure 3a), EDX elemental maps of Al (Figure 3b), Cu (Figure 3c), O (Figure 3d), Fe (Figure 3e) and Ti (Figure 3f), and quantitative EDX analysis of the regions (EDX 1, EDX 2) as marked in Figure 3a (Figure 3g, h) (Figure 3i, j), across the interface between Al₂O₃ substrate and Al-1.4Cu alloy.

Figure 3h is enlarged from Figure 3g. Figure 3j is enlarged from Figure 3i. Clearly, a significant Cu segregation at the interface between Al_2O_3 substrate and Al-1.4Cu alloy was observed, as shown in Figure 3c and Figure 3h, j, although the Cu concentration (about 2.5 at %) obtained in EDX1 is slightly higher than that (about 1.5 at %) in EDX 2, which can be attributed to the surface roughness of Al_2O_3 substrate. The significant Cu segregation can be attributed to twofold: the enhanced diffusion caused by the high strain with large lattice misfits (9.45 %) and the chemical reaction between Al_2O_3 substrate and Al-1.4Cu alloy. Similar to Figure 2, a very trace Fe and Ti was also observed, which can be attributed to the impurities induced during the sample melting process (arc melting).

In order to further elucidate the details of the interface, Figure 4 shows enlarged HAADF-STEM micrograph (Figure 4a), EDX elemental maps of Al (Figure 4b), Cu (Figure 4c), O (Figure 4d), and quantitative EDX analysis of the total region in Figure 4a (Figure 4e, f) across the interface between Al_2O_3 substrate and Al-1.4Cu alloy. Figure 4f is enlarged from Figure 4e. Similar to Figure 3, a significant Cu segregation (about 2.0 at %) at the interface between Al_2O_3 substrate and Al-1.4Cu alloy was observed, as shown in Figure 4c, f. It should be noted here that the Cu concentration (about 2.0 at %) in Figure 4 is taken from the total region (Figure 4a), which can be regarded as an average value. Furthermore, similar to Figure 3, a very trace Fe and Ti was also observed (Figure 4e, f).

The strain at the interface is one of the key factors affecting the heterogeneous nucleation. For the relatively large lattice misfits, the maximum energy dissipated through introduced misfit dislocation may be not sufficient. The rest of strain energy will, therefore, be reserved in the layer and forming planar defects, such as micro-twins [11]. In this study, a

lower lattice misfit system (9.45 %) was deliberately created. The strain energy may be able to dissipate through introducing lattice dislocation, as predicted in [8]. Therefore, dislocation with a high number density was observed, as shown in Figure S2. As proposed in [8], the strained layer takes atomic structure from substrate. After the strain energy is released, the strained layer normally vanishes. However, the presence of the dislocation will definitely enhance the diffusion of Cu at the interface. Furthermore, once the Cu segregation is sufficient enough, the chemical reaction between Al_2O_3 substrate and Al-1.4Cu alloy may occur, as shown in Figures 3, 4. By forming the intermetallic (i.e. Al_2Cu), heterogeneous nucleation can be suppressed.

In summary, we have investigated the Cu segregation at the interface between Al_2O_3 substrate and Al-1.4Cu alloy by HAADF-STEM imaging and EDX. A significant Cu segregation (about 2 at %) was observed, which can be attributed to twofold: the enhanced diffusion caused by the high strain with large lattice misfits (9.45 %) and the chemical reaction between Al_2O_3 substrate and Al-1.4Cu alloy. This investigation highlights the importance of Cu segregation on the heterogeneous nucleation of Al on Al_2O_3 substrate.

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Comment [JL3]: Please add your acknowledgments here.

References

1. J. Dantzig, M. Rappaz, Solidification, CRC Press, Lausanne, 2009.
2. K.F. Kelton, A.L. Greer, Nucleation in Condensed Matter, Elsevier, Oxford, 2010.
3. A.L. Greer, A. Bunn, A. Tronche, P. Evans, D. Bristow, Acta Mater. 48 (2000) 2823.
4. T.E. Quested, A.L. Greer, Acta Mater. 53 (2005) 2683.
5. W. Kim, B. Cantor, Acta Metall. Mater. 42 (1994) 3115.
6. Q. Ma, Acta Mater. 55 (2007) 943.
7. L. Wang, L. Yang, D. Zhang, M. Xia, Y. Wang, J. Li, METALLURGICAL AND MATERIALS TRANSACTIONS A 47 (2016) 5012.
8. Z. Fan, METALLURGICAL AND MATERIALS TRANSACTIONS A 44 (2013) 1409.
9. G. Wilde, C. Santhaweesuk, J.L. Perepezko, Acta Mater. 54 (2006) 4759.
10. P. Schumacher, A.L. Greer, Mater. Sci. Eng. A 178 (1994) 309.
11. L. Yang, M. Xia, J. Li, IOP Conf. Series: Materials Science and Engineering 117 (2016) 012002.
12. A.J. Brown, H.B. Dong, P.B. Howes, C.L. Nicklin, Scripta Mater. 77 (2014) 60.
13. S.H. Oh, Y. Kauffmann, Scheu, W.D. Kaplan, M. Ruhle, Science 310 (2005) 661.
14. S.B. Lee, Y.M. Lee, Acta Mater. 59 (2011) 1383.
15. M. Gradman, Y. Kauffmann, C.T. Koch, W.D. Kaplan, Phys. Rev. Lett. 110 (2013) 086106.
16. L. Yang, M.X. Xia, N.H. Babu, J.G. Li, Materials Transactions, 56 (2015) 277.
17. H.T. Li, Y. Wang, Z. Fan, Acta Mater. 60 (2012) 1528.
18. B.L. Bramfitt, Metall. Trans. 1 (1970) 1987.

Fig. 1: Bright field TEM micrographs (a, c) and corresponding selected area electron diffraction (SAED) (b, d) across the interface between Al_2O_3 substrate and Al-1.4Cu alloy. (a, b) Al_2O_3 substrate was tilted to [011] zone axis. (c, d) Al matrix was tilted to [011] zone axis. Clearly, there is no orientation relationship between Al_2O_3 substrate and Al matrix. The impurities (Ti, Fe) within the Al matrix can be related to the melting process (arc melting).

Fig. 2: HAADF-STEM micrograph (a), EDX elemental maps of Al (b), Cu (c), O (d), Ti (e), Fe (f) across the interface between Al_2O_3 substrate and Al-1.4Cu alloy. Cu-rich phase (very likely to be Al_2Cu phase formed during the solidification) was observed within the Al matrix, as shown in (c). It should be noted here that Ti was also observed, which can be attributed to the impurities induced during the sample melting process (arc melting). However, it is not believed to play a significant effect on the nucleation of Al on the Al_2O_3 substrate.

Fig. 3: HAADF-STEM micrograph (a), EDX elemental maps of Al (b), Cu (c), O (d), Fe (e) and Ti (f), quantitative EDX analysis of the regions (EDX 1, EDX 2) as marked in (a) (g, h) (i, j), across the interface between Al_2O_3 substrate and Al-1.4Cu alloy. (h) is enlarged from (g). (j) is enlarged from (i). A significant Cu segregation at the interface between Al_2O_3 substrate and Al-1.4Cu alloy was observed, as shown in (c) and (h, j), although the Cu concentration (about 2.5 at %) obtained in EDX1 is slightly higher than that (about 1.5 at %) in EDX 2, which can be attributed to the surface roughness. As described in Figure 2, a very trace Fe and Ti was also observed, which can be attributed to the impurities induced during the sample melting process (arc melting). However, it is not believed to play a significant effect on the nucleation of Al on the Al_2O_3 substrate.

Fig. 4: Enlarged HAADF-STEM micrograph (a), EDX elemental maps of Al (b), Cu (c), O (d), quantitative EDX analysis of the total region in (a) (e, f) across the interface between Al_2O_3 substrate and Al-1.4Cu alloy. (f) is enlarged from (e). Similar to Figure 3, a significant Cu segregation (about 2.0 at %) at the interface between Al_2O_3 substrate and Al-1.4Cu alloy was observed, as shown in (c) and (f). It should be noted here that the Cu concentration (about 2.0 at %) in Figure 4 is taken from the total region (a), which can be regarded as an average value. Furthermore, similar to Figure 3, a very trace Fe and Ti was also observed (e, f), which can be attributed to the impurities induced during the sample melting process (arc melting).