The interface of heterogeneous nucleation on single crystal substrates

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Abstract. Under controlled nucleation process was achieved by solidifying a high purity Al droplet on a single crystal Al 2 O 3 substrate in a high vacuum chamber. The following X-Ray Diffraction (XRD) analysis and measured undercooling prove that the nucleation was triggered by the substrate. Various lattice mismatches between new crystal and substrate (C/S) were obtained through this approach. Combining XRD patterns and high resolution transmission electron microscope analysis we found that the morphology of interface was affected by lattice misfit. An epitaxial layer was found at C/S interface with larger lattice misfit, as in Al(100)/Al 2 O 3(0001) system. Further experiments on introduced alloying element, Sb, into liquid Al shows a suppressed epitaxial layer of Al. Chemical reaction between liquid and substrate also contributes to the formation of the interface. The nucleation of Al on the MgO substrates was actually nucleated on MgAl 2 O 4, chemical reaction product of Al and MgO, rather than MgO.

1. Introduction
Nucleation has been focused on for about 200 years since the pioneering investigation of Fahrenheit [1] on the solidification tendency of supercooled water. However, due to the limitation on time resolution of examine approaches [2], there was no direct observation results on nucleation process so far until the study on the nucleation of protein apoferritin [3]. A few relevant studies on the ordering of liquid structure adjacent to liquid-solid (L/S) interface were believed to be able to disclose how the nucleation starts. For instance, S.H. Oh et al. [4] provided the evidence for the ordering of liquid Al atoms adjacent to L/S interface by knocking oxygen atoms out of α-Al 2 O 3 wafer. Lee and Kim [5] proved the ordering structure adjacent to Al 2 O 3 contains oxygen rather than being a pure Al layer. Gandman et al. [6] pioneered the research to the ordering degree of the layer which varies as a function of adjacent crystal planes. However, even though the ordering structure was proved to be adjacent to S/L interface, there is no solid evidence for nucleation starting from the ordering structure.

In most of the cases, the studies on nucleation focus on its kinetics, thermodynamics and even numeric or analogue simulations [7]. P. Schumacher et al. [8,9] investigated the crystallization of amorphous Al alloy on TiB 2 substrates in order to demonstrate the heterogeneous nucleation of Al alloy. They found a layer of Al 3 Ti at Al/TiB 2 interface. Based on their results, it was well recognized now that the heterogeneous nucleation of Al catalyzed by TiB 2 is through the formation of Al 3 Ti layer. But high resolution transmission electron microscopy (HRTEM) analysis shows there are only one or two layers of Ti-contained structure adjacent to the interface. Thus, it is hardly to identify atomic structure of the layer. Fan [10] proposed an hypothesis assuming that heterogeneous nucleation of liquid metal initiates from epitaxial growth, where a strained layer will develop before new crystal forms. The hypothesis is in line with previous L/S interface results. The strained layer takes atomic
structure from substrate, called pseudomorphic solid (PS) layer. The strain energy of PS layer is closely related to the lattice misfit between new crystal and substrate (C/S) and will be released through the development of misfit dislocations or planar defects. After the strain energy released, the strained layer normally vanishes. So there is no evidence for the existence of PS layer based on the hypothesis.

Since the strain energy of epitaxial layer is related to the lattice misfit of C/S interface, we will enlarge the lattice misfit deliberately in this study so that the strained layer can be reserved after nucleation given the strain energy large enough to overcome the energy released by misfit dislocation. Alloying element effect and chemical reaction effect are also concerned as factors affecting nucleation interface in this study.

2. Experimental
In order to focus on lattice misfit effect on nucleation, the substrates with different crystal planes (0001), (10-10), (11-20), (1-102) are cut from one single crystal \( \alpha \)-Al\(_2\)O\(_3\). High purity Al (99.999wt\%) was purified using glass fluxing method to remove potential heterogeneous nuclei from liquid Al. Intrinsic undercooling of pure Al was examined on levitation apparatus in a high vacuum chamber to reduce the interference of the container, which is in turn to be compared with the undercooling of liquid Al solidified on substrates. By the comparison, we can suggest whether the nucleation is triggered by the substrates or not. X-ray diffraction (XRD) analysis was employed to detect the nucleation surface of new crystal from the bottom of the sample where nucleation was triggered by the substrates. The lattice misfit calculation follows Bramfitt equation [11]. Parameters of new crystal for calculation were taken from the plane with preferred orientation. The details can be referred to ref.[12]. Furthermore, alloying element, Sb, was added into liquid Al with 1wt\% to examine the alloying element effect on the nucleation interface. Single crystal MgO were used to replace Al\(_2\)O\(_3\) substrates to demonstrate chemical reaction effect.

Nucleation behaviour of the liquid metal was detected through high speed camera. Undercooling was recorded using a pyrometer with an accuracy of \( \pm 1 \) K and a time resolution of 50 \( \mu \)s. The thin foils for transmission electronic microscopy (TEM) and HRTEM were prepared from cut slices perpendicular to C/S interface with a thickness less than 80 \( \mu \)m before ion beam thinned using a Gatan precision ion polishing system (PIPS) at 5.0 kV and an incident angle of 4-6\( ^\circ \). A Tecnai G2 F20 S-twin TEM instrument was used for TEM, HRTEM and energy dispersive X-ray spectroscopy (EDS) analyses with an accelerating voltage of 200 kV.

3. Results

3.1. Substrate interfered heterogeneous nucleation
Figure 1 shows typical undercooling measured from levitation experiment and from the sample solidified on single crystal substrates. It reveals that the undercooling of liquid Al solidified on the substrate was smaller than the levitation sample. The latter has a 44.4 \( ^\circ \)C after glass fluxing treatment, while the sample solidified on single crystal substrate only has 23.8 \( ^\circ \)C undercooling. The difference between these two experiments indicates that the substrate interfered the nucleation of liquid Al. Furthermore, XRD patterns of the samples solidified on different substrates also prove solidification was affected by the substrate (as shown in figure 2). The preferred orientation detected on nucleation surface varies with the exposed plane of the substrate.
3.2. Interface with various lattice misfits

Due to the substrates effect on the preferred orientation of nucleation surface, parameters for lattice misfit calculation were selected from the crystal plane with preferred orientation. The calculated misfits are listed in figure 2. The interface between Al crystal and Al$_2$O$_3$ substrates with different crystal planes were presented in figure 3. For the samples with larger lattice misfit, for instance Al(100) solidified on Al$_2$O$_3$(0001), there is a dark plate growing from the interface towards Al side while for the sample with smaller lattice misfit, there is only a distinctive interface without any perturbation. Misfit also affects the shape of the plate. For the interface with larger misfit, the plate is wider and flat while with smaller misfit, the plate is thicker but slightly narrow like a platform standing on the interface. HRTEM analysis on the plate shows that there is large amount of planar defects in the plate (figure 4). Select area electron diffraction (SAED) at the interface shows both Al$_2$O$_3$ pattern and an unknown phase as indexed. Combining both atomic lattice image and SAED patterns in figure 4, the unknown phase could be a micro-twin structure. EDS result proves the plate is composed of pure Al.

**Figure 1.** Cooling curves of levitation sample and the sample solidified on the substrate showing the nucleation of liquid Al was affected by the substrate.

**Figure 2.** XRD patterns of the nucleation surface of the sample solidified on different substrates. The relevant lattice misfits obtained from XRD results are list as well.

**Figure 3.** The C/S interfaces with different lattice misfit (a) Al(100) // Al$_2$O$_3$(10-10), (b) Al(100) // Al$_2$O$_3$(1-102), (c) Al(100) // Al$_2$O$_3$(0001), (d) Al(311) // Al$_2$O$_3$(11-20) showing the larger lattice misfit will produce epitaxial layer.
3.3. Interface with alloying element

1wt% Sb was added into pure Al to investigate the alloying element effect on the nucleation behaviour of Al alloy. XRD patterns of the nucleation surface were presented in figure 5. Comparing with XRD pattern of pure Al, the peaks changed after adding 1wt% Sb. Al (311) peak detected on Al\textsubscript{2}O\textsubscript{3} (11-20) substrate for pure Al was replaced by Al (111) and Al (220) with a few AlSb peaks accompanying. But on Al\textsubscript{2}O\textsubscript{3} (0001) substrate, the strongest peak was altered to Al (220) only comparing with (111) and (200) without Sb addition. Thus, the alloying element does modify nucleation behaviour of liquid Al. Apart from the preferred orientation of nucleation surface, the epitaxial layer adjacent to the C/S interface was also suppressed as shown in figure 6.

![Figure 4](image1.png)

**Figure 4.** (a) HRTEM image and (b) SAED patterns of epitaxial layer show large amount of planar defects in the layer, which is composed of Al micro-twins.

![Figure 5](image2.png)

**Figure 5.** XRD patterns of Al-1wt%Sb nucleated on Al\textsubscript{2}O\textsubscript{3} (11-20) and Al\textsubscript{2}O\textsubscript{3} (0001) substrates

![Figure 6](image3.png)

**Figure 6.** TEM picture of the Al/Al\textsubscript{2}O\textsubscript{3} interface showing a suppressed perturbation occurs adjacent to the interface and Al side shows typical poly-crystal feature.
3.4. Interface with chemical reaction
Due to the chemical reactivity of liquid Al on MgO substrate, single crystal MgO was selected as substrates to investigate the effect of chemical reaction on heterogeneous nucleation. The preferred orientation of nucleation surface is presented in figure 7. Apart from an additional Al (220) peak on MgO (111) substrate, Al (111) peak was found as a preferred orientation in all three samples. The relevant misfit for each sample is marked in figure 7. Undercooling on different substrates are relatively equal within the margin of error (figure 8). It does suggest that “misfit effect” may not affect the nucleation of Al on MgO. Further investigation on C/S interface found a Zigzag interface replacing the original interface between Al and MgO as shown in figure 9. HRTEM and SAED pattern analysis prove this zigzag layer is MgAl2O4 with (111) plane exposed to Al. Thus, whichever the single crystal MgO substrate was selected in the study, the nucleation only occurs on MgAl2O4 substrate with (111) exposed plane, which subsequently lead to an average undercooling in figure 8.

4. Discussion
4.1. Formation of epitaxial layer
The dissipation of strain energy in PS layer is the key factor affecting whether PS layer vanishing or not after nucleation. In this study, large lattice misfits (16.4% and 33.8%) were deliberately created by introducing single crystal substrate Al2O3 into Al nucleation process. The expected strain energy is no less than 574 Jm^-2 for Al2O3 (11-20) substrate, which can be calculated according to [13] while based on dislocation theory [14]. The maximum energy that can be dissipated through introduced misfit dislocation is only about 0.964 Jm^-2, much less than the energy need to be dissipated. The rest of strain energy will be reserved in the layer and forming planar defects, as micro-twins in this study. For lower lattice misfit system, the strain energy is much less and will be able to dissipate through introducing lattice dislocation, as predicted by Fan [10], et al.

4.2. Type of heterogeneous nucleation interface
However, due to the interference of the interface reaction, the morphology of the interface also varies. With low lattice misfit, the interface of C/S is distinctively clean, without any perturbation. Further enlarging misfit of C/S, perturbation will be found due to the undissipated strained atomic layer, as so called epitaxial layer in this study. Lattice misfit also affect the morphology of epitaxial layer as shown in figure 3 c and d. Apart from lattice misfit, alloying element and chemical reactive substrate
also take some effect on heterogeneous nucleation interface. Alloying element affects the preferred orientation of new crystals. But due to the new formed intermetallics, perturbation or epitaxial layer can be suppressed as shown in figure 6. In addition, chemical reaction changes the morphology of the interface. For instance, MgO reacted with Al forming MgAl$_2$O$_4$ layer between Al and MgO which replaced MgO as new substrate. In general, there are 4 typical interfaces presented in this study:

- Interface without perturbation with smaller C/S misfit.
- Interface with epitaxial layer with larger C/S misfit.
- Interface with suppressed perturbation after adding alloying element.
- Eroded interface by chemical reaction.

![Figure 9](image)

**Figure 9.** (a) TEM image of Al nucleated on MgO substrate showing a zigzag interface produced by chemical reaction. (b) Indexed SAED patterns of the layer show the pattern presenting MgAl$_2$O$_4$ feature.

5. Conclusions

Various heterogeneous nucleation interfaces were demonstrated in this study. The effect of C/S misfit on nucleation interface was investigated through a controlled nucleation process, which proves epitaxial layer can be reserved after solidification by using substrate with larger lattice misfit with new crystal. After adding alloying element, epitaxial growth will be suppressed since the introduced alloy element may change preferred orientation of the new crystals. Chemical reaction is another factor playing an important role on the interface of heterogeneous nucleation. In Al-MgO system, chemical reaction product, MgAl$_2$O$_4$ replaced MgO as new substrate.

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