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The Heterogeneous Nucleation Sequence at the Interface of TiB_2 in Al Alloys

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Refinement of Al alloys by TiB_2 has been extensively studied in both industry and academia for several decades [1-10]. The presence of solutes (*e.g.* Ti) enhances the TiB_2 grain refinement potency by tailoring the heterogeneous nucleation interface of TiB_2 [10]. To date, there is still a lack of atomic scale experimental investigations of the heterogeneous nucleation interface of TiB_2 under industrial solidification conditions (*e.g.* conventional die casting). In order to address these open issues, a combination of atomic scale high angle annular dark field (HAADF) imaging and electron energy loss spectroscopy (EELS) in the dedicated aberration corrected scanning transmission electron microscope (STEM) is used for the characterization of the heterogeneous nucleation interface of TiB_2 in Al alloys, with a special focus on the partitioning of non-interacting solute elements (*e.g.* Ti and Cu) to TiB_2. Experiments were carried out on two distinct material systems in order to more accurately elucidate the multiple roles of Ti in Al alloys and to determine the dominant mechanism for grain refinement in Al alloys. Firstly, as a reference, the heterogeneous nucleation interface of TiB_2 in a commercial Al-Ti-B grain refiner (*i.e.* Al-5Ti-1B) was studied. Secondly, the grain refinement of Al-Cu based alloys with varying Ti content (but with identical growth restrictions to the reference case) was investigated. The heterogeneous nucleation interface of TiB_2 in Al-Cu based alloys was also studied. The effect of the solidification path (*i.e.* a peritectic reaction and a subsequent peritectic transformation) on the observed nucleation phenomena is also discussed.

Figure 1 shows a significant partitioning of Ti to the surface of TiB_2 in the commercial grain refiner (Al-5Ti-1B). During solidification, the presence of a Ti-rich monolayer is strongly dependent on the solidification path. This is because the Ti-rich monolayer can potentially be consumed by a peritectic reaction. Figure 2 shows that Ti partitioning is present together with a significant Cu-rich monolayer (most likely Al_2Cu) on the surface of the TiB_2 particle, in an Al-Cu based alloy. The above discussed Ti and Cu rich monolayers were observed over the whole surface of the respective TiB_2 particles. A nucleation sequence on the basal plane of TiB_2 is proposed. Firstly, Al nucleation occurs on an Al_3Ti monolayer. Secondly, the Al_3Ti monolayer is preserved from the subsequent peritectic transformation by a surrounding eutectic reaction layer that forms Al_2Cu on Al. Based on this nucleation sequence, the absence or presence of an Al_3Ti monolayer on the basal plane of TiB_2 can be interpreted. The present work provides a clearer picture of the heterogeneous nucleation interface between TiB_2 and Al and demonstrates that an Al_3Ti monolayer must be present if the grain refinement is growth-limited. Only then can growth restriction and concentration undercooling play their full part.

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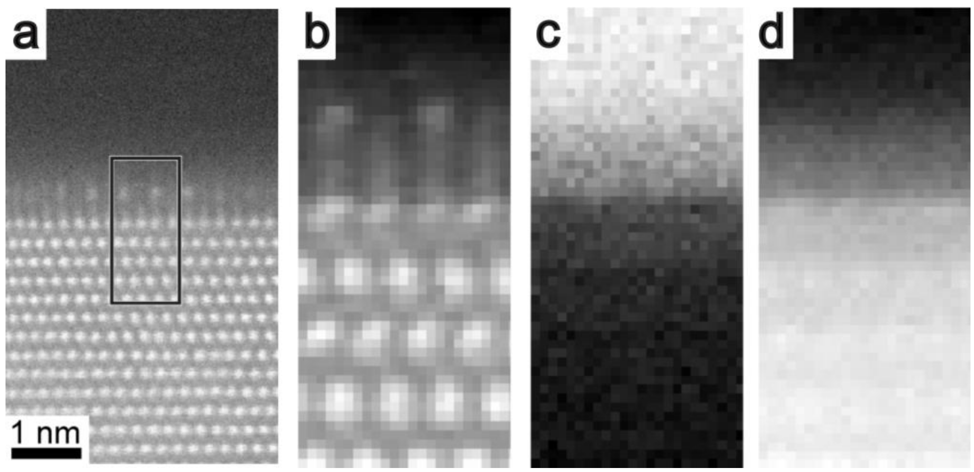

Figure 1. HAADF STEM images (a, b) and EELS maps of Al (c) and Ti (d) in the commercial Al-5Ti-1B grain refiner. The data is taken from the basal plane of TiB_2. (B//<1-21-3>$_{TiB2}$)

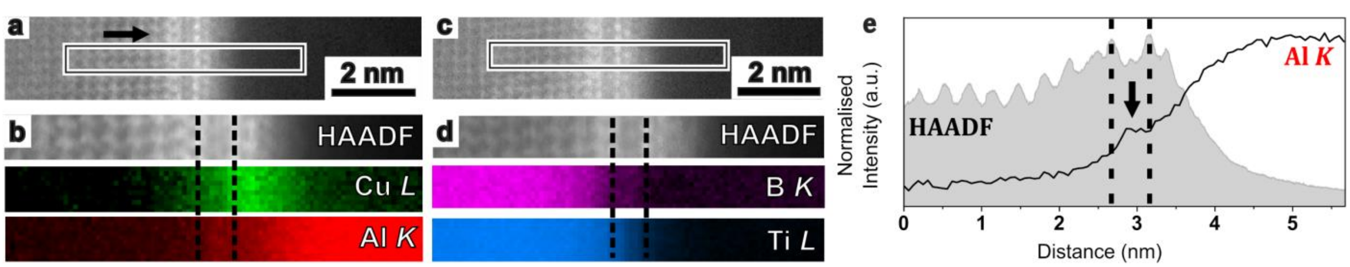

Figure 2. HAADF STEM images (a) (c) and EELS maps of Al and Cu (b), Ti and B (d) of TiB_2 particle in the Al-Cu based alloy with the identical growth restriction of 19.6 K. (e) A line scan across the interface, as indicated by the black solid arrow in (a). The data is taken from the basal plane of TiB_2. (B//<11-20>$_{TiB2}$)

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