Elemental segregation at substrate/metal interface to manipulate heterogeneous nucleation

Dr Shihao Wang[1,2,3], Dr Yun Wang[3], Dr Zhongyun Fan[3], Dr Quentin Ramasse[1,2]
[1]SuperSTEM Laboratory, STFC Daresbury Campus, Daresbury WA4 4AD, United Kingdom, [2]School of Chemical and Process Engineering, University of Leeds, Leeds LS2 9J, United Kingdom, [3]BCAST, Brunel University London, Uxbridge, Middlesex UB8 3PH, United Kingdom

Background incl. aims

Heterogeneous nucleation on a substrate in a metallic melt is a fundamental step in tailoring the microstructure of engineering materials with desired properties, and therefore it is a research topic of critical scientific and technological importance to meet the goals of the 'circular economy' [1]. The structural and chemical compatibility at a substrate/metal-liquid interface dictates the heterogeneous nucleation process. This can be altered by elemental interfacial segregation, affecting the nucleation behaviour accordingly [2]. Atomic-scale interfacial segregation has been linked to the successful application of TiB2-based grain refiners for aluminium casting, also explaining some of their limitations depending on the nature of segregation structure [2,3]. Interfacial segregation has also been applied as a strategy to modify native oxides in aluminium and magnesium alloys, whereby naturally occurring oxides can then be harnessed for grain refinement [2,4]. Studies of the microstructure and composition across the substrate/metal interface, down to the atomic scale, are thus essential in determining nucleation potency.

Advances in aberration-corrected scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS) now routinely allow for both atomic-resolution imaging and compositional analysis of materials. In this work, we use advanced STEM-EELS to investigate different substrate/metal interfaces including TiB2/Al, MgO/Mg, and γ-Al2O3/Al in the corresponding casting alloy ingots of different grain refinement performances, aiming to provide an overview of our atomic-level understanding of the behaviour of interfacial segregation and its resultant effect on heterogeneous nucleation and grain refinement.

Methods

Casting experiments were used to evaluate the grain refinement. Pressurized melt filtration was applied to different alloy melts to collect the inoculant particles, by which the possibility of substrate/metal interface appearing in a TEM foil specimen is greatly increased for characterization. STEM imaging and EELS acquisition were performed on a Nion UltraSTEM100 scanning transmission electron microscope, equipped with a Gatan Enfina EELS spectrometer retrofitted with a MerlinEELS direct electron detector. The microscope was operated at an accelerating voltage of either 100 or 60kV, depending on the beam sensitivity of the observed structures, with the probe-forming optics configured for a 31mrad convergence semi-angle and a probe size of 1Å or smaller.

Results

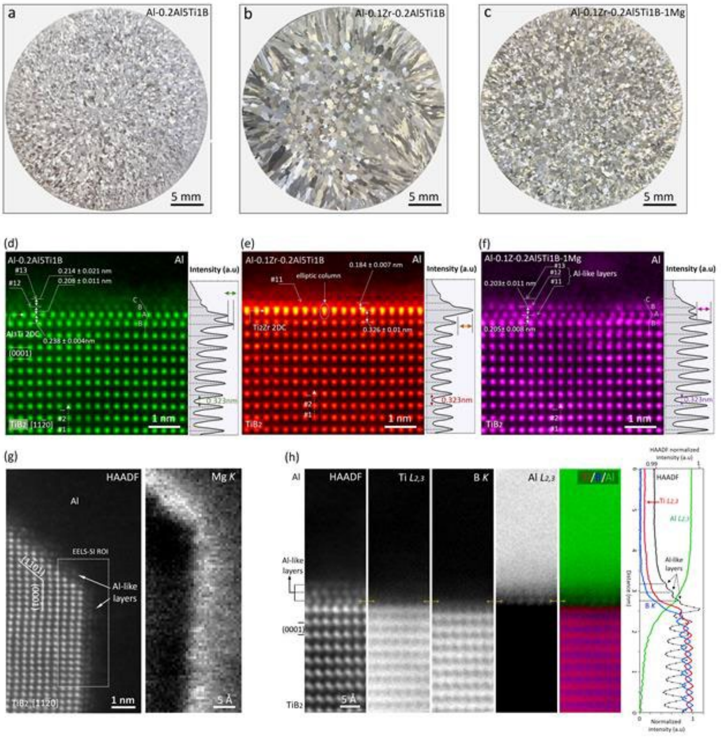
High-precision high-angle annular dark field (HAADF) STEM imaging and EELS mapping offer an atomic-level view of how interfacial segregation affects the grain refining performance in model alloy systems, with an example of the TiB2/Al system shown in Figure 1. Rigid- or non-rigid registration were applied to series of (spectrum) images, taken with short dwell times and along different zone axes, to reveal the precise structure and chemistry of an atomically thin, so-called Al3Ti 2-dimensional compound (2DC) segregation layer at the interface between inoculant TiB2 particles and Al matrix: figure 1d. This structure was shown to account for the grain refinement achieved in an Al-0.2Al5Ti1B alloy. Similarly, a Zr-segregation-induced Ti2Zr 2DC (figure 1e) is atomically resolved at the interface, which poisons the grain-refining effect of TiB2: a coarse and columnar grain structure forms in Al-

0.1Zr-0.2Al5Ti1B. Interestingly, the grain refinement behaviour is rejuvenated after the addition of Mg (Al-0.1Zr-0.2Al5Ti1B-1Mg), which results in the dissolution of the poisoning Ti2Zr 2DC and the formation of hitherto never-observed Mg-rich layers adopting a local structure similar to bulk Al, and thus termed Al-like layers (figure 1f-h). Analysis of the electron energy loss near-edge fine structure (ELNES) provides additional information regarding the valence state and/or electronic structure of these interfacial structures, for instance confirming the nature of the 'Y-O' bonding within a Y-rich segregation layer at the MgO/Mg interface [4].

Conclusion

Atomic-resolution STEM-EELS has provided conclusive evidence to clarify the role of interfacial 2DCs in determining the nucleation potency of TiB2 and thus the grain refining performance. With the high spatial resolution and single-electron-sensitive EELS detector, advanced STEM-EELS is expected to be a powerful tool in understanding heterogeneous nucleation, designing grain refiners, and controlling solidification structures and mechanical properties across a wide range of metallic materials.

Graphic:



Keywords:

Interfacial segregation, STEM/EELS, Solidification

Reference:

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