The nature of native oxides in Mg with various alloying elements

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Minimising and even eliminating the detrimental effects caused by native oxide inclusions is one of the major tasks in recycling of Mg alloys. Our current research demonstrates that native oxide particles formed in-situ in Mg alloy melts can be harnessed for promoting heterogeneous nucleation, resulting in grain refinement.

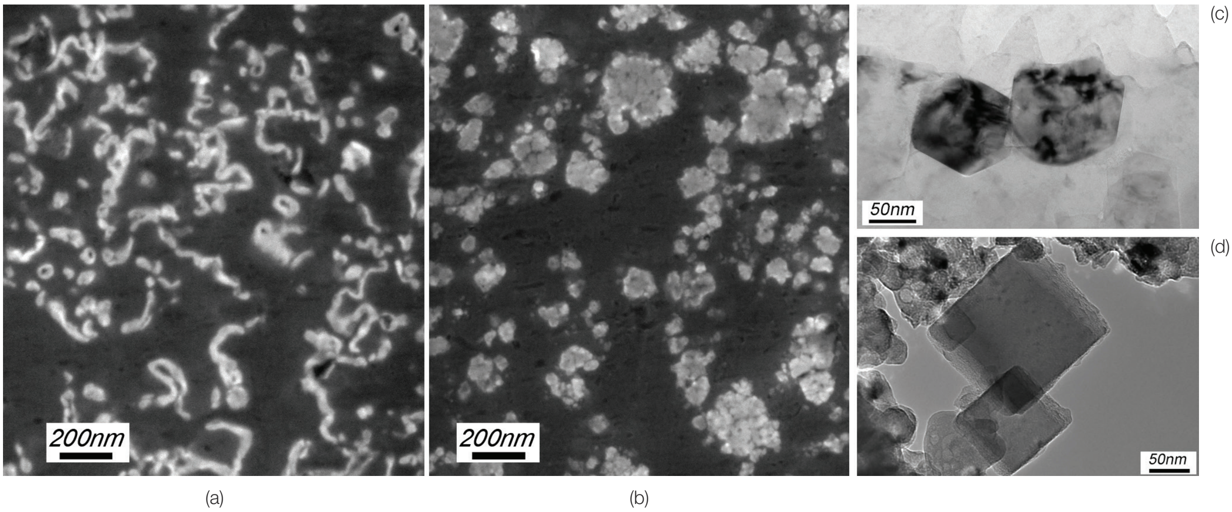

FIGURE 1. SEM and TEM images showing the diverse morphology of the native MgO particles formed in Mg and Mg-9Al alloy with (a) string-like, (b) cauliflower-like, (c) decahedral, and (d) cubic.

However, commercial Mg alloys usually contain many alloying elements which are essential to promote the performance of the alloys. Addition of such elements are expected to affect the nature of the in-situ oxides, and in turn the potency for heterogeneous nucleation and finally the effectiveness of grain refinement for Mg alloys. Therefore, there is a need to comprehensively understand the formation mechanism and growth behaviour of oxides in Mg alloy melt as well as the effect of alloying elements.

Controlled oxidation experiments were carried out with the native oxide films/particles being collected using pressurised melt filtration technology. The state-of-the-art electron microscopy was carried out to examine the oxides at atomic scale. Figure 1 shows the diverse morphology of the MgO particles collected from commercial purity Mg and Mg-9Al alloy melts. The morphology can be classified as decahedral, cubic, string-like and cauliflower-like, with the average size being 65 nm and 82 nm for pure Mg and the alloy respectively. The cubic {100} faceted MgO was formed because of burning at high temperature, indicating the minimum surface energy on its {1 0 0} crystal planes. However, the majority of MgO particles in AZ91D (Mg-Al based) alloy is {1 1 1} faceted. It is also revealed that the cauliflower shaped MgO was attributed to the effect of nitrogen and fluorine from the protection atmosphere during processing. 0.5 wt% addition of yttrium to commercial purity Mg resulted in the formation of oxide films consisting of both MgO and Y_2O_3 particles, with their morphology being cubic and decahedral as well. The oxide particles in the rare-earth element containing Mg melts show a larger size, about 120 nm in average, although some smaller (~50 nm in size) particles were also observed. With MgO and Y_2O_3 particles being frequently associated each other, high resolution TEM revealed that there is specific relationships between them, i.e., {1 1 1}MgO and {0 0 1}Y_2O_3.

It has demonstrated that formation and growth behaviour of native oxide particles in Mg and its alloys are significantly affected by alloying elements and the protection atmosphere during processing of the melts. When the oxide particles are harnessed to act as heterogeneous nucleation sites, such diversity in the morphology and size will significantly affect the nucleation process, resulting in advanced effectiveness for grain refinement of Mg alloys.

A comprehensive study is being performed to understand the mechanisms underlying the effect of the important alloying elements in Mg alloys, including Al, Zn, Ca, Sn as well as a small amount of rare earth elements. Any segregation of the elements on the surfaces of the oxides is to be studied. Further investigations will be focused on the effect of the native oxide particles on heterogeneous nucleation. This will include diverse morphology and size distribution for the oxides.