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FIB serial milling and lifting out of fine inclusions in an intensively melt sheared aluminum alloy ☆

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ABSTRACT

An intensively melt sheared aluminum alloy was cast to verify the possibility of heterogeneous nucleation of aluminum grains from fine oxide particles. A novel combined technique of serial milling and lifting out using the focused ion beam has detected fine particles at the grain center of aluminum. High resolution analytical electron microscopy shows that oxides can act as substrates for the nucleation of aluminum grains. Based on the observations, the possibility of survival and nucleation potency of the oxide is discussed.

1. Introduction

Surface of molten aluminum–magnesium alloys is continuously oxidized due to their high oxygen affinities at high temperature. In casting, the turbulence of melt stirring and pouring easily fractures and entrains the oxides into a melt, which affects the mechanical properties and corrosion resistance of cast metal alloys by the formation of porosity and hot tearing [1]. Recently, it was suggested that grain refinement of cast aluminum alloys might be induced by the enhanced heterogeneous nucleation of aluminum grains from fine and well dispersed oxides in the melt which was intensively sheared before solidification [2,3]. However, there is little agreement on the heterogeneous nucleation on oxides due to, generally, poor wettability and high contact angles of liquid aluminum and oxides [4]. Furthermore, since the oxide size and its volume fraction in an intensively sheared melt are too small to detect and analyze with scanning electron microscopy (SEM), it has been considered impossible to detect directly and prove the effect of oxides on the heterogeneous nucleation during solidification. An alternative technique using the pressurized melt filtration was used to collect and concentrate the oxide particles for high resolution analyses [3,5]. However, this filtration technique might not reflect all solidification related phenomena of the intensively sheared melt occurring in a real mould due to the different cooling rate and its effect on the grain size and non-equilibrium phase(s) [4]. Therefore, it is imperative to detect and observe the oxides existing in an actual cast sample which was intensively sheared and simultaneously showed a uniform microstructure as well as fine grains.

2. Experimental

An aluminum alloy (AA 5754 alloy with the composition of Al-3.12Mg-0.05Si-0.5Fe-0.43Mn-0.001Cu-0.02Ti, wt%), which showed the possibility of enhanced heterogeneous nucleation of aluminum grains from fine particles after intensive shearing [2], was used and melted in a clay graphite crucible at 1028 K. For the intensive shearing, the melt was poured into the melt conditioning unit at 953 K, and melt conditioned at 500 rev/min at 928 K for 60 s by twin screws. Then, the intensively sheared sample was cast using a laboratory scale horizontal twin roll caster, which has been described in detail elsewhere [2].

Metallographic sections for SEM were prepared using standard grinding and polishing procedures, and etched by a solution (100 ml distilled water, 4 g potassium permanganate, 1 g sodium hydroxide). Microstructural observations were then carried out with the focused ion beam (FIB) SEM (FIB-SEM, FEI Quanta 3D dual beam) equipped with an electron dispersive X-ray spectrometer (EDX), and high resolution transmission electron microscopes (TEM, FEI Tecnai F20 with a scanning mode (STEM) and an EDX, and JEOL JEM-2100FCS with a spherical aberration (C_s) corrector as well as a STEM mode and an EDX).

3. Results and discussion

Several studies showed that the particle which acted as a substrate for heterogeneous nucleation of a primary grain should

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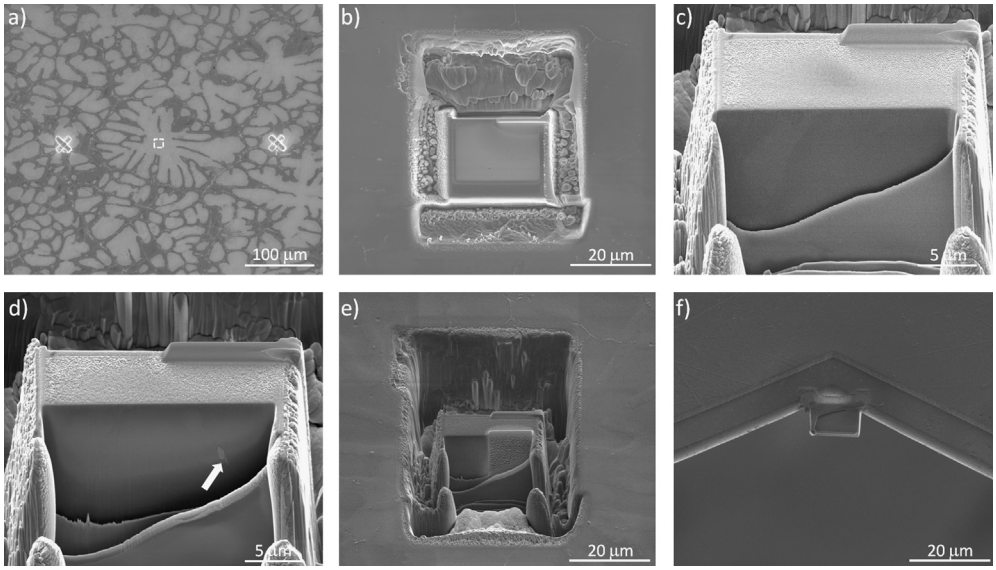

Fig. 1. Procedure of serial sectioning and TEM sampling to find a fine inclusion.

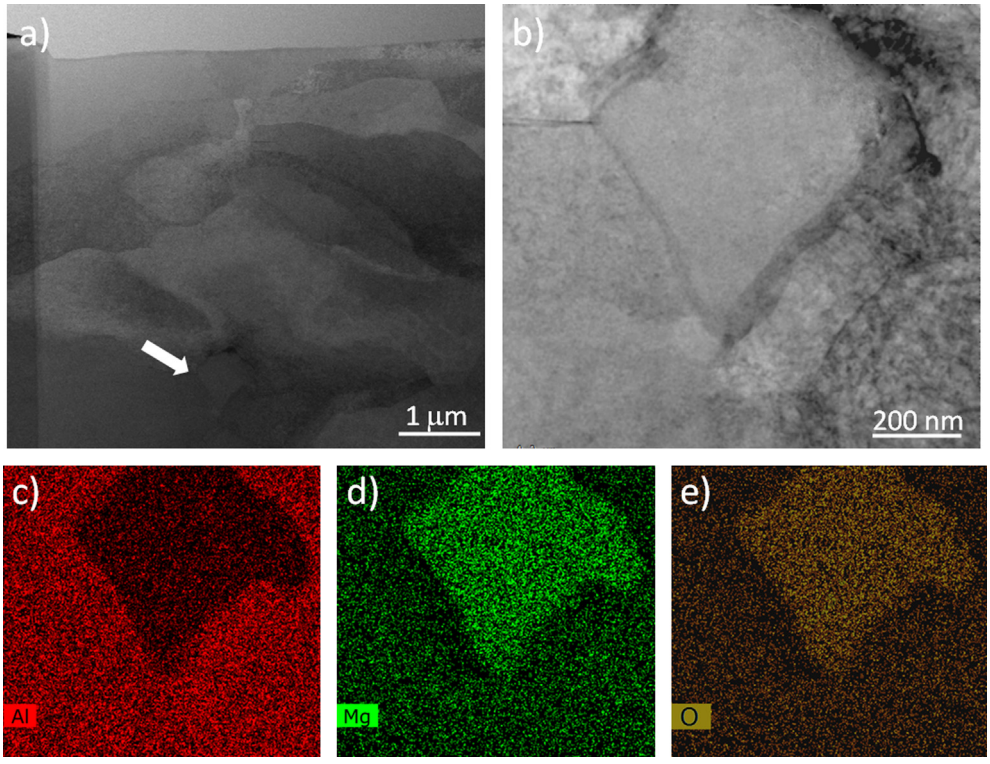

Fig. 2. STEM BF images ((a) and (b)) and corresponding element mappings of aluminum (c), magnesium (d), and oxygen (e) of the particle detected in Fig. 1.

exist at/near the grain center [6,7]. Therefore, FIB serial sectioning combined with a lift-out technique was designed to detect the inclusion and to remove any artifacts during cutting, grinding and polishing. Fig. 1 shows the procedure to find and make a TEM sample from an inclusion. A grain between two 'X's intentionally marked by FIB was selected and a thin tungsten layer of about 2 μm was deposited on the area of about $20 \times 15\ \mu m^2$ at the grain center to protect the surface from strong ion beam during serial sectioning (Fig. 1a). The region surrounding the tungsten deposited area was milled away as shown in Fig. 1b. Then, the cross section was serial-milled with a milling step of about 200 nm until finding a fine particle. After each milling step, the milled region was observed meticulously by secondary electron beam (Fig. 1c). After additional milling of about 3 μm, finally, different contrast became visible in the ion beam milled region (see the arrow in Fig. 1d). On observing the fine particle, the serial milling stopped and an additional protective tungsten layer was deposited on the surface (Fig. 1e). A lamella including the particle was put on a copper grid (Fig. 1f). Then, a thin foil for TEM study was exquisitely fabricated using a FIB lift-out technique [8,9].

Fig. 2 shows STEM images and element mappings of the particle detected in Fig. 1. Even though the quality of STEM bright field (BF) images is a bit poor due to the thickness of the lamella

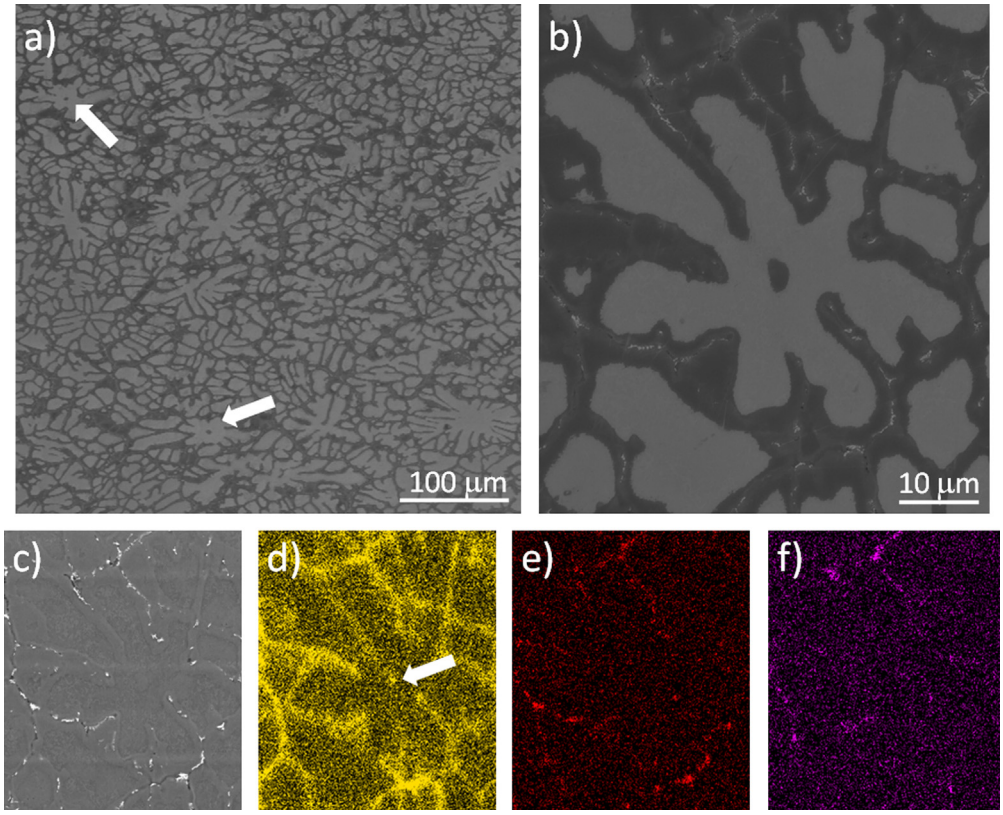

Fig. 3. SEM analysis of a fine particle at the center of an aluminum grain. The arrows in panel (a), respectively, indicate a fine particle at the center of each grain.

and some remaining gallium on the surface, the particle indicated by an arrow in Fig. 2a is clearly composed of magnesium and oxygen. A point chemical analysis of STEM-EDX using a C_s-corrected probe with the size of 1 nm confirmed the magnesium oxide (see also Fig. 4). It is interesting to find magnesium oxide (MgO) not spinel ($MgAl_2O_4$), which might act as a substrate for heterogeneous nucleation of an aluminum grain.

In order to detect another particle at/near the center of other aluminum grains, the surface of the intensively sheared sample was carefully polished and etched by the solution, and then observed by a field emission SEM with an EDX system. Fig. 3 shows another particle detected at the center of an aluminum grain. At the center, different contrast is visible (Fig. 3a and b). A backscattered electron (BSE) image (Fig. 3c) and a SEM-EDX element mapping of magnesium (see the arrow in Fig. 3d) clearly show high amounts of magnesium at a particle located on the grain center as well as at grain boundaries. Since the solubility of alloying elements or impurities with a negative slope of the liquidus line and a partition coefficient of below 1, such as magnesium, iron, and silicon in this study, is larger in liquid aluminum than in solid, solute elements are rejected from the growing grains and enriched ahead of them [10]. Thereby, iron (Fig. 3e) and silicon (Fig. 3f) as well as magnesium are enriched where the liquid completes solidification, and finally precipitate at cell and grain boundaries, as shown clearly in Fig. 3.

For TEM analysis of the particle showing the high amount of magnesium, the FIB lift-out technique was used to make a TEM sample. Fig. 4 shows STEM images and EDX point analyses of the particle in Fig. 3. The STEM-EDX spectra acquired by a fine probe of 1 nm confirm that the particle indicated by an arrow in Fig. 4a is composed of only magnesium and oxygen. Therefore, although several studies suggested that the stable oxide might be $MgAl_2O_4$ [3,5], the particle which acted as the substrate for heterogeneous nucleation of aluminum grains is magnesium oxide.

Based on classical nucleation theory, it is important to achieve good lattice match by small disregistry ($\delta = \Delta a_0/a_o$), where Δa_0 is the difference between lattice parameters of a nucleant and a nucleating metal with the same crystal structure along a specific direction, and similar crystallography for a low interfacial energy between them [7,11]. According to this criterion, MgO as well as $MgAl_2O_4$ have high nucleation potency for aluminum grains ($a_0 = 0.4121$) because both have low lattice mismatches of MgO ($a_0 = 0.4213$, $\delta = 2.2\%$) and $MgAl_2O_4$ ($0.5a_0 = 0.4375$, $\delta = 4.1\%$) and the same face-centered cubic structure [12]. Compared to $MgAl_2O_4$, however, MgO forms more easily due to the higher reactivity of magnesium than aluminum [13]. A recent study using Al-4%Mg showed that a porous MgO layer with the thickness of about 5 μm forms at a short oxidation time of 5 min and the thickness gradually increases to about 7 μm for 1 h [14]. Thereafter, $MgAl_2O_4$ may be formed by the reaction of $2MgO_{(s)} + 4Al_{(l)} + 3O_{2(g)} = 2MgAl_2O_{4(s)}$. However, it is interesting that X-ray diffraction (XRD) patterns of an Al-10%Mg alloy oxidized for 3 h show peaks corresponding to MgO [15]. McLeod and Gabryel also presented a thermodynamic stability diagram of Al–Mg oxides showing that MgO is more stable than $MgAl_2O_4$ for high magnesium concentrations of above 1.5% at 1028 K [15]. In addition, as $MgAl_2O_4$ exists in the alloy melt as discrete particles due to low Pilling–Bedworth ratio [3], the melt containing aluminum and magnesium can rise into capillary $MgAl_2O_4$ tubes and reoxidize to form MgO, repeatedly. It was accordingly concluded that MgO can survive during melting and intensive shearing, and may act as a substrate for heterogeneous nucleation of aluminum grains during solidification.

The potency of nucleants for the heterogeneous nucleation has been evaluated by the interfacial free energy. However, the interface energy is influenced by the chemical nature, electrostatic potential, and misfit dislocations in the interface of a nucleant and a nucleated metal [11,16]. Therefore, the change in the density of bonds across the interface as well as the crystallographic

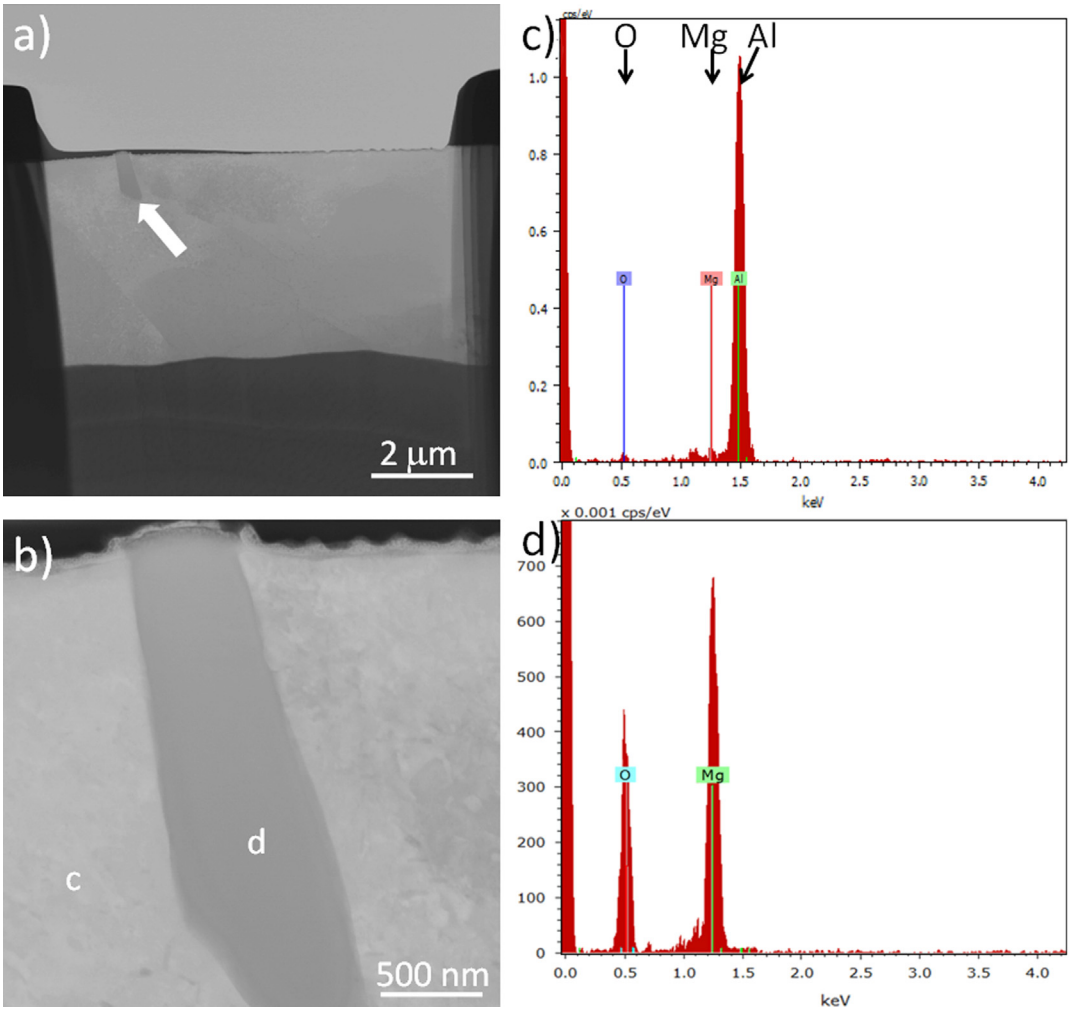

Fig. 4. STEM BF images ((a) and (b)) and STEM-EDX point analysis ((c) and (d)) at the marked regions in panel (b) of the fine particle found in Fig. 3, respectively. The panel (b) is a magnified image including the particle.

relationship of a nucleant and a nucleated metal should be considered to evaluate the potency. In this criterion, MgO has high potency because the interface of oxygen-terminated MgO and aluminum has strong bonds induced by the ionic component and covalent/metallic contribution, which are primarily determined by the electron density of oxygen atoms at the top-layer of MgO [17]. The potency as well as the survival of MgO will be further discussed elsewhere.

4. Summary

Heterogeneous nucleation of aluminum grains on fine oxide particles has been suggested to explain the grain refinement observed in an intensive shearing process. A FIB technique using lifting-out and serial-sectioning successfully detected fine oxide particles at/near aluminum grains. The oxide has high potency of the heterogeneous nucleation due to strong ionic and covalent/metallic bonds at the interface as well as the good crystallographic match of MgO and aluminum.

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