Impurity effects on the solidification of primary $\text{Al}_3(\text{Sc,Zr})$ phase in $\text{Al}$ alloys

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Abstract. The nucleation and growth of primary $\text{Al}_3\text{Sc}$ phase has been investigated in high purity $\text{Al}$ alloys and commercial purity $\text{Al}$ alloys, with a special focus on the impurity effects. In the case of high purity $\text{Al}$ alloys, most primary $\text{Al}_3\text{Sc}$ phases were pushed to grain boundaries during moving solidification front. Such type of primary $\text{Al}_3\text{Sc}$ phase does not contribute to the heterogeneous nucleation and thereby no significant grain refinement of $\text{Al}$ alloys was observed, although some $\text{Al}_3\text{Sc}$ particles remain the same orientation with the $\text{Al}$ matrix. In the case of commercial purity $\text{Al}$ alloy, the presence of impurities, e.g. $\text{Ti}$, $\text{Fe}$ and $\text{Si}$, enhances the heterogeneous nucleation of primary $\text{Al}_3\text{Sc}$ phase. Most primary $\text{Al}_3\text{Sc}$ phases are located within the $\text{Al}$ matrix, and keep the same orientation with the $\text{Al}$ matrix. Furthermore, the presence of impurities also changes the growth mode of primary $\text{Al}_3\text{Sc}$ phase. In the case of commercial purity $\text{Al}$ alloy, a layer by layer growth was observed. This investigation demonstrates that impurities have important effects on the nucleation and growth of primary $\text{Al}_3\text{Sc}$ phases in $\text{Al}$ based alloys.

1. Introduction

In the early 1960s, the potential of Sc in controlling microstructure of $\text{Al}$ based alloys has been recognized [1, 2]. Significant improvements in properties of commercial 5xxx, 7xxx have been achieved through Sc additions. Most previous research focused on the decomposition of supersaturated $\text{Al}-\text{Sc}$ solid solutions, which leads to the formation of the fully coherent, secondary $\text{L}_1_2 \text{Al}_3\text{Sc}$ phase. However, much less attention has been paid to the primary $\text{Al}_3\text{Sc}$ phase solidified directly from the liquid. Although Sc only exhibits a small growth restriction in $\text{Al}$ alloys, even smaller grain sizes than with $\text{Al}$-$\text{Ti}$-$\text{B}$ grain refiner addition can be obtained with hypoeutectic addition of Sc into $\text{Al}$ based alloy. The grain refinement effect may be mainly dominant by heterogeneous nucleation. Furthermore, grain refinement by Sc addition was found to be accompanied by a change in growth morphology from unrefined dendritic, to fine spherical grains with a divorced eutectic appearing on the grain boundaries in the refined castings [3].

In order to further decrease the expensive Sc addition, a combined addition of Zr and Sc was found to enable a considerable grain refinement in $\text{Al}$ alloys, which is much stronger than that of Zr or Sc alone. Furthermore, an important impurity effect has been reported in [4-6]. The presence of such types of the impurities (i.e. Fe, Si) affects the nucleation and growth of primary $\text{Al}_3(\text{Sc,Zr})$ phase, and thereby enhance the heterogeneous nucleation of $\alpha$-$\text{Al}$ during solidification.

In this paper, the nucleation and growth of primary $\text{Al}_3(\text{Sc,Zr})$ phase has been investigated in high purity $\text{Al}$ alloys and commercial purity $\text{Al}$ alloys, with a special focus on the impurity effects. The nucleation and growth modes are also discussed.
2. Experimental methods

High purity Al-0.25Sc-0.25Zr alloy was prepared using high purity Al ingots (5N, 99.998), Al-10 wt. % Zr and an Al-2.2 wt. % Sc master alloys (wt. %, used throughout the paper unless noted otherwise), respectively. For comparison, commercial purity Al-0.25Sc-0.25Zr alloy was also prepared using commercial purity Al ingots (2N8, 99.8), Al-10Zr and an Al-2.2Sc master alloy, respectively. It should be noted that in high purity Al, Si (7 ppm), Fe (6 ppm), Cu (8 ppm), Mg (4 ppm), Ti (< 1 ppm) were measured in high purity Al. While, in commercial purity Al, Si (0.0675), Fe (0.805), Cu (0.0011), Mg (0.0113), Ti (0.0117) were measured in commercial purity Al. Clearly, significant impurities (Si, Fe, Mg, Ti) are present in commercial purity Al alloys.

Each batch, weighting about 6 kg, was melted in a resistance furnace at 720 ºC. A reference sample was taken from the melt in order to identify the grain size before the additions of Al-10Zr and Al-2.2Sc master alloys. The melt was stirred with a graphite rod for 20 s after inoculation. The samples were taken from the melt after the addition of Al-10Zr and Al-2.2Sc master alloys (about 5 min) and tested using standard TP-1 test.

According to the TP-1 test, the samples were sectioned 38 mm from the bottom surface. Standard metallographic procedures were performed to prepare these sections for grain size measurements. The samples were etched using a mixture of 13 g boric acid, 35 g HF, 800 ml H₂O at a voltage of 20 V for 45 seconds. All images used for grain size measurement were taken from the centre of the samples using optical microscopy in a polarized mode. The reported grain sizes were measured from at least 20 images using the line-intersect method.

The samples for scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) investigation were mechanically ground and electron-polished in a solution consisted of 5% perchloric acid and 95% methanol at -30 ºC. EBSD investigation was performed using a Zeiss 1525 scanning electron microscope equipped with an EDAX EBSD system. Evaluation of scans was made with orientation imaging microscopy (OIM) software. The EBSD investigation can be used to determine the orientation relationship between the primary Al₃(Sc,Zr) particles and the α-Al matrix. In order to further elucidate the enrichment of the impurities, electron probe micro analyzer (EPMA, JEOL JXA-8500F) was also employed.

3. Results

Figure 1 shows one primary Al₃(Sc,Zr) particle in high purity Al alloy with the addition of 0.25Sc and 0.25Zr. The primary Al₃(Sc,Zr) particle is located at the grain boundaries, as marked in figure 1a. However, the local region of the primary Al₃(Sc,Zr) particle is located within the α-Al matrix, as enlarged in figure 1b. Such kind of primary Al₃(Sc,Zr) phases is believed to be engulfed during solidification. No low angle orientation relationship (e.g. cube to cube) was observed between the primary Al₃(Sc,Zr) particle and the α-Al matrix, indicating that this pro-eutectic Al₃(Sc,Zr) particle did not contribute to the heterogeneous nucleation and thereby grain refinement. A coarse grain size was observed, as marked in figure 1c.
Figure 1. Primary Al$_3$(Sc,Zr) phase in high purity Al alloy.

Figure 2. Primary Al$_3$Sc phase with a layer by layer growth in commercial purity Al alloy.
Figure 2 shows one primary Al\textsubscript{3}(Sc,Zr) particle in commercial purity Al alloy with the addition of 0.25Sc and 0.25Zr. The “star-like” primary Al\textsubscript{3}(Sc,Zr) particle was found to be located within the α-Al matrix. The orientation of the primary Al\textsubscript{3}(Sc,Zr) particle is identical to the orientation of the α-Al matrix [7]. Such type of primary Al\textsubscript{3}(Sc,Zr) phase is believed to contribute to the heterogeneous nucleation during solidification. A fine grain size was observed, as shown in figure 2b. Furthermore, a very interesting observation is that the primary Al\textsubscript{3}(Sc,Zr) particle appears to grow layer by layer, as shown in figure 2a. Some layers with a weaker contrast were observed. These layers are believed to be enriched in impurities (e.g. Si, Fe, Cu, Mg, Ti), which are always present in commercial purity Al alloys. In fact, the layered structure is typical for commercial purity Al alloys with Sc and Zr addition.

In order to further elucidate the enrichment of the impurities within the layered structure, figure 3 shows a series of EPMA mapping. Clearly, Al is enriched in the α-Al matrix between the layers of the Al\textsubscript{3}(Sc,Zr) phase. While, Sc, Ti and Zr are enriched in the Al\textsubscript{3}(Sc,Zr) phase. It should be noted that, similar to Al, other impurities (i.e. Cu, Si, Fe) may be also present in the α-Al matrix between the layers of the Al\textsubscript{3}(Sc,Zr) phase [8].

![Figure 3](image-url)

Figure 3. A series of EPMA mapping of primary Al\textsubscript{3}Sc phase in commercial purity Al alloy.
4. Discussions
The final grain size of Al alloy is dependent on the number density, size and size distribution of primary Al$_3$(Sc,Zr) phases and the growth restriction of Al. The growth restriction of Al alloy is dependent on the cooling rate, liquid flow field and growth restriction factor of the alloying elements. In this study, the cooling rate, liquid flow field can be regarded to be identical because the standard TP-1 test was performed. As there is also little influence of growth restriction on Al caused by Zr, Sc addition and only low addition of other elements, the factors affecting the final grain size is mainly by the number density, size and size distribution of primary Al$_3$(Sc,Zr) phases. The number density, size and size distribution of primary Al$_3$(Sc,Zr) phases itself is dependent on the impurity and the growth restriction on Al$_3$(Sc,Zr) phase. The presence of impurities (i.e. Si (0.0675), Fe (0.805), Cu (0.0011), Mg (0.0113), Ti (0.0117) in commercial purity Al-0.25Sc-0.25Zr alloy results into significant effects on the number density size and size distribution of primary Al$_3$(Sc,Zr) particles [7].

The observed layered structure of the Al$_3$(Sc,Zr) particle can be discussed on the basis of the solidification sequence [8]. Firstly, by a peritectic reaction, the faceted Al$_3$(Sc,Zr) phase forms. Once the peritectic particle has formed further solidification is by the peritectic reaction: Al$_3$Zr + liquid → Al, which leads to the formation of the first Al layer. This Al layer can act as nucleation surface for the initial eutectic reaction: liquid → α-Al + Al$_3$Sc(X) where the second phase (here Al$_3$Sc) has to be formed. The very close orientation relationship and small mismatch between Al and Al$_3$Sc permits readily nucleation of Al$_3$Sc on Al. The subsequent eutectic reaction occurs within the diffusion field of rejected elements (i.e. Al) not participating easily in the peritectic or eutectic reaction. This subsequent eutectic transformation cannot occur readily as the Al-Al$_3$Sc is a heavily divorced eutectic system so that no cooperative growth is seen but there are subsequent eutectic reactions of Al$_3$Sc on Al and Al on Al$_3$Sc. However, this growth by subsequent eutectic reactions is hindered by other elements present in the diffusion field surrounding the growing particle. In order to avoid long range diffusion other elements are incorporated into a ternary cell structure with the Al$_3$Sc(X) layer. While the Al layer can easily accommodate the solute elements present. This peritectic growth mechanism can terminate until the eutectic transformation ends and the last Al layer has reached a critical size at which free growth for a given undercooling occurs [9-11].

5. Conclusions
In the case of high purity Al alloys, primary Al$_3$(Sc,Zr) particles were pushed to grain boundaries by the moving solidification front. Such type of primary Al$_3$(Sc,Zr) phase did not contribute to the heterogeneous nucleation, and thereby grain refinement of Al alloys. In the case of commercial purity Al alloy, the presence of impurities not only enhances the heterogeneous nucleation of primary Al$_3$(Sc,Zr) phase, but also induced a transition on primary Al$_3$(Sc,Zr) phase from a peritectic to eutectic reaction. This investigation demonstrates that impurities have important effects on the nucleation and growth of primary Al$_3$(Sc,Zr) phases and subsequently on Al in Al alloys. Controlling impurities and their concentrations can enhance the grain refinement of Al alloys.

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