ATOMIC OBSERVATION ON THE SOLUTE ADSORPTION AND ENTRAINMENT DURING Si GROWTH IN Al-Si BASED ALLOYS

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ABSTRACT

The solute adsorption and entrainment of Sr, Na and Yb during Si growth in a series of high purity melt spun Al-5 wt.% Si alloys was investigated by atomic resolution high angular annular dark filed imaging in an aberration corrected scanning transmission electron microscope. The adsorption of Sr or Na atoms was observed at the twin plane re-entrant edge and at the intersection of Si twins, which can be used to interpret the well-known poisoning of twin plane re-entrant edge and impurity induced twinning modification mechanisms. In contrast, the segregation of Yb atoms was distinguished to be different from the adsorption of Sr or Na atoms along the $\{111\}_{Si}$ growth planes. The absence of Yb within Si, in particular at the twin re-entrant edges or at the intersection of Si twins, was related to a refinement, rather than a modification of eutectic Si in Al-Si alloys.

1. INTRODUCTION

Modification of eutectic Si in Al-Si alloys can be dated back to 1920 [1], since the first modification phenomenon was discovered by Pacz. Recent technological developments of electron microscopy, e.g. high resolution transmission electron microscopy (HRTEM), high resolution scanning transmission electron microscopy (HRSTEM) and atom probe tomography (APT), make it possible to investigate the modification mechanisms at an atomic scale. To date, it is generally accepted that impurity induced twinning (IIT) [2] and twin plane re-entrant edge (TPRE) growth mechanism [3, 4], as well as poisoning of the TPRE [5] are valid under certain conditions. However, neither IIT, TPRE, nor poisoning of the TPRE can be used to interpret all the previous modification observations [6-9]. For example, Yb addition into Al-Si alloys has been reported to only refine, rather than modify, the eutectic Si [6], even though Yb atom has an exactly suitable radius ratio (r_{Yb} / r_{Si} = 1.646) according to the IIT mechanism. The observed disagreements strongly indicate that the well-accepted IIT mechanism, based on the atomic radius alone, is not capable of explaining the modification of eutectic Si, and additional mechanisms are still expected to be active. Therefore, a revision of the solute adsorption and entrainment of modifiers during modification of eutectic Si is thus of great necessity to elucidate this important melt treatment for Al-Si based alloys.

In this paper, the solute adsorption and entrainment during eutectic Si growth in a series of high purity Al-5 wt.% Si alloys with Sr, Na and Yb additions were investigated, with a special focus on the distribution of Sr, Na and Yb atoms within eutectic Si, in particular along the $<112>_{Si}$ growth direction of Si and at the intersection of multiple Si twins.

2. EXPERIMENTAL MATERIAL AND PROCEDURES

A series of Al-5 wt. % Si alloys (wt. %, used through the paper, in case not specified otherwise) with the additions of Sr (200 ppm), Na (160 ppm) and Yb (6100 ppm) were prepared using conventional die casting. Sr and Yb additions were made by using Al-4Sr and Al-5Yb master alloys. Na was added using elemental Na in vacuum packed Al foils before casting.

TEM samples were mechanically ground, polished and dimpled to about 30 μm, and then ion-beam milled using a Gatan Precision Ion Polishing System (PIPS, Gatan model 691). High resolution TEM were performed using a Cs-corrected JEOL-2100F microscope operated at 200 kV. The high resolution STEM were performed using a monochromated and probe corrected FEI Titan^{3TM} G2 60-300 (S/TEM) microscope operated at 300 kV with an X-FEG high brightness emission gun.

3. RESULTS

3.1 Al-5Si ALLOY WITH Sr ADDITION

Figs. 1b, d, f show a series of scanning transmission electron microscopy high angular annular dark filed (STEM-HAADF) images of multiply twinned Si particles and Al-Si-Sr-rich particles in an Al-5Si-200 ppm Sr alloy. In order to elucidate the location of Sr atoms within eutectic Si, corresponding dark field images are also shown in Figs. 1a, c, e. Multiply twinned Si particle were observed. As expected from poisoning of the TPRE and IIT mechanisms, Al-Si-Sr-rich clusters were observed along the $<112>_{Si}$ growth direction of Si (Fig. 1d) and at the intersection of two $\{111\}_{Si}$ twins (Fig. 1f), respectively. Al-Si-Sr-rich particles with a size of about 20 nm were also observed within the Si particle, which can be attributed to the possible solute entrainment during eutectic Si growth, as discussed in section 4.

3.2. Al-5Si ALLOY WITH Na ADDITION

Similar to the Sr addition (Fig. 1), Na addition (up to 160 ppm) into Al-5Si alloy also promotes a significant increase of Si twins, as shown in Fig. 2. After tilting to the principal twinning orientation of Si ($<011>$), both parallel Si twins and multiple Si twins were observed. Such type of Si twins can be attributed to poisoning of the TPRE mechanism and IIT mechanism, respectively. Furthermore, the number density of Si twins appears to be much higher than that in Al-5Si alloy with 200 ppm Sr addition, indicating a higher adsorption tendency of Na atoms than Sr atoms along the $<112>_{Si}$ growth direction of Si and at the intersection of Si twins. It should be noted that no attempt was made to take STEM-HAADF image and to elucidate the location and distribution of Na within eutectic Si, because of the fact that the atom numbers between Al, Si and Na are very close (Z_{Na} = 11, Z_{Al} = 11, Z_{Si} = 14). The brightness contrast of Na is considerably less strong than that of Sr (Z_{Sr} = 38). However, a similar behaviour, i.e. the adsorption of Na atoms along the $<112>_{Si}$ growth direction of Si and at the intersection of two $\{111\}_{Si}$ twins as well as the possible solute entrainment during eutectic Si growth, can be expected.
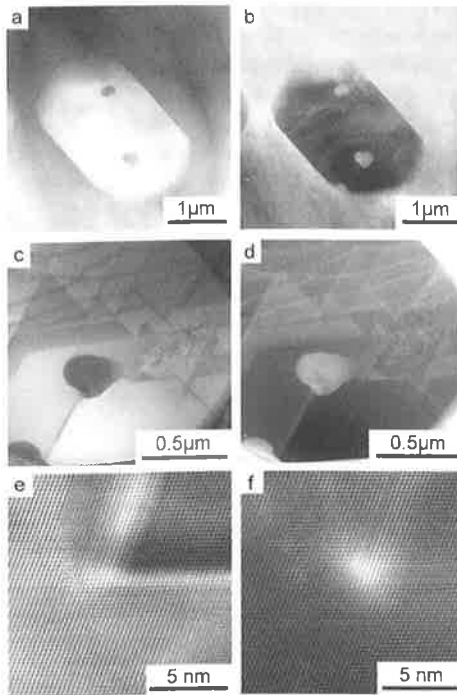
Fig. 1: (a), (c), (e) Dark field images, (b), (d), (f) STEM-HAADF images taken from Al-5Si-200 ppm Sr alloy, (c), (d) are enlarged from (a), (b), showing the Al_2Si_2Sr particle within Si, (e), (f) are enlarged from (c), (d), showing the Sr-rich clusters along the $<112>_{Si}$ growth direction of Si and at the intersection of Si twins. B // $[011]_{Si}$.
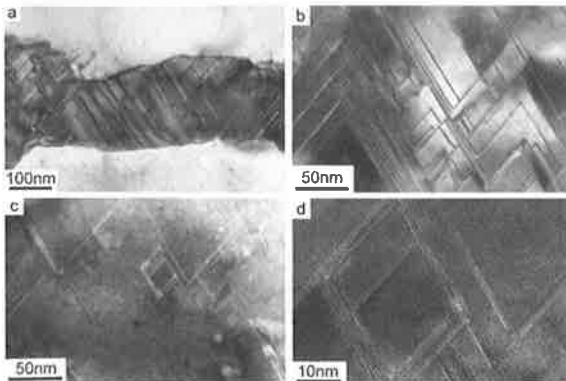

Fig. 2: A series of high resolution TEM images taken from Al-5Si-160 ppm Na alloy, (b), (c), (d) are enlarged from (a), showing the Na-rich particle within Si and the Na-rich clusters along the $<112>_{Si}$ growth direction of Si and at the intersection of Si twins. B // $[011]_{Si}$.

3.3. Al-5Si ALLOY WITH Yb ADDITION

The addition of Yb (up to 6100 ppm) into Al-5Si alloy has no significant effect on Si twinning, when compared to the additions of Sr (up to 200 ppm) (Fig. 1) and Na (up to 160 ppm) (Fig. 2). Fig. 3 shows a faceted Si particle tilted to the <011> zone axis along the grain boundary in Al-5Si-6100 ppm Yb alloy. Unexpectedly, no significant Si twinning was observed, despite the favourable atom size ratio according IIT mechanism. This observation is in contrast to the prediction of IIT mechanism. Furthermore, no significant Yb-rich cluster was observed along the $<112>_{Si}$ growth direction of Si and at the intersection of Si twins (Fig. 3d). No Al_2Si_2Yb particle was observed within eutectic Si because no significant solute adsorption and / or entrainment of Yb atoms occur during eutectic Si growth. Instead, most Al_2Si_2Yb particles were observed adjacent the Si phase (Fig. 3a, b), strongly indicating that most Yb atoms segregate out of eutectic Si.
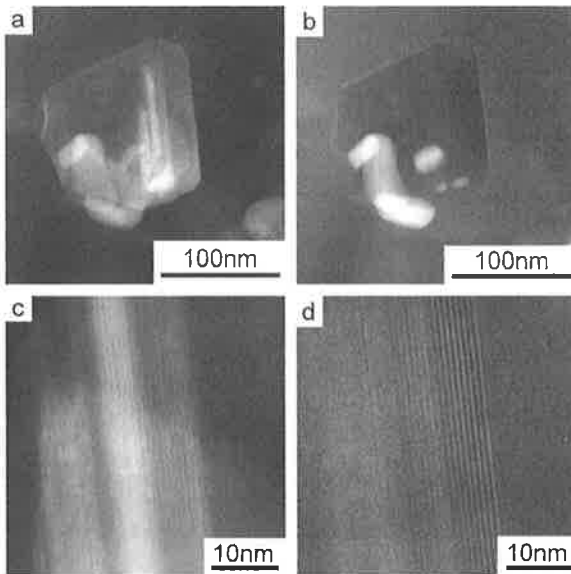

Fig. 3: (a), (c) Dark field images, (b), (d) STEM-HAADF images taken from Al-5Si-6100 ppm Yb alloy, (c), (d) are enlarged from (a), (b), showing no significant Yb-rich cluster and thereby Si twinning within Si. B // $[011]_{Si}$.

4. DISCUSSIONS

Fig. 4 shows a schematic representation of the Sr solute adsorption and / or segregation as well as the possible solute entrainment ahead of solidification front of eutectic Si in Al-Si alloys. In the liquid state, the alloying elements (i.e. Al, Sr and Si) are randomly distributed, although solute clustering (i.e. Si clustering) may occur. During eutectic Si growth (Fig. 4a), Sr and Al solute will segregate ahead of the solidification interface ($k_{Al} < 1$ and $k_{Sr} < 1$). A solute redistribution of Sr and Al, and thus an enrichment of Sr and Al ahead of the solidification front may occur. During continuous Si growth, the adsorption of Sr atoms on $\{111\}_{Si}$ plane occurs along the $<112>_{Si}$ growth direction of Si and / or at the intersection of two $\{111\}_{Si}$ twins (Fig. 4b). According to the poisoning of the TPRE, the adsorption of Sr

along the $<112>_{Si}$ growth direction of Si promotes the formation of further parallel Si twins with a higher number density. According to the IIT mechanisms, the adsorption of Sr at the intersection of two $\{111\}_{Si}$ twins promotes the formation of multiply Si twins.
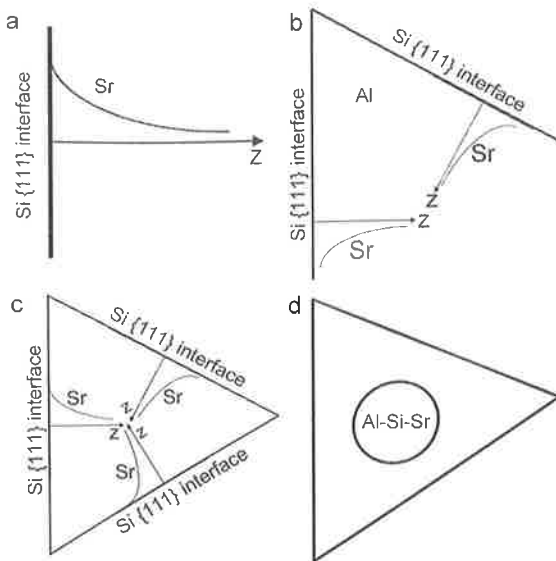

Fig. 4: Schematic representation of the adsorption of Sr atoms along the $<112>_{Si}$ growth direction of Si and at the intersection of Si twins, forming Si twinning, and the solute entrainment of Sr atoms, forming Al_2Si_2Sr particle within eutectic Si. (a) Equilibrium solidification, (b) The adsorption of Sr atoms occurs along the $<112>_{Si}$ growth direction of Si and at the intersection of Si twins, forming Si twinning, (c) Sr adsorption occurs along other $<112>_{Si}$ growth direction of Si and at other intersection of Si twins, forming parallel or multiply Si twinning, (d) Sr solute entrainment occurs, forming Sr-rich clusters, finally Al_2Si_2Sr particle within eutectic Si.

The adsorption of Sr atoms at the intersection of Si twins and / or along the $<112>_{Si}$ growth direction can also occur during further eutectic Si growth, which may also yield further re-entrant edges of Si twinning or a change of stacking sequence of Si twinning (Fig. 4c). In this case, eutectic Si growth will re-start from another $\{111\}_{Si}$ plane. Similarly, an enrichment of Sr and Al atoms in a local area and another multiple Si twinning occurs. Finally, once the $\{111\}_{Si}$ planes fold on each other, the solute impingement and subsequent entrainment of the segregation fields occurs (Fig. 4d). On subsequent cooling, the solute entrainment forms Al-Si-Sr-rich particles with different morphologies and compositions, which are mostly likely to be Al_2Si_2Sr phase if the cooling rate is low enough, or the segregation time and length is sufficient enough.

The proposed solute entrainment can be used readily to interpret the observation of the Al-Si-Sr-rich clusters in present investigation and previous reports using APT [8]. The observed Al-Si-Sr-rich clusters can be an "artefact" caused by solute entrainment, rather than an active factor affecting the modification. However, the observed Al-Si-Sr-rich clusters exhibits the position of the solute adsorption and subsequent entrainment during eutectic Si growth, i.e. along the $<112>_{Si}$ growth direction of Si and / or at the intersection of two $\{111\}_{Si}$ twins. Therefore, it is proposed that the adsorption of Sr is a dominant factor

for modification of eutectic Si in Al-Si alloys. While, the observed Al-Si-Sr-rich clusters with different sizes and compositions are caused by the solute segregation and thereby the solute entrainment of Sr atoms, which were formed during eutectic Si growth, rather than the first and dominant step to lead to poisoning of the TPRE and IIT growth mechanisms.

In contrast to the cases of Sr addition, no significant multiple Si twins was observed in the case of Yb addition. Because of the absence of Yb atoms along the $<112>_{Si}$ growth direction of Si and at the intersection of two $\{111\}_{Si}$ twins, Yb addition (up to 6100 ppm) appears not to promote the formation of the parallel or multiple Si twinning (Fig. 3). If any, only single Si twinning can be observed, which is similar to the case of Al-5Si based alloy caused by natural TPRE. Furthermore, no Al_2Si_2Yb particle was observed within eutectic Si because no significant solute adsorption and / or entrainment of Yb atoms occurs during eutectic Si growth. Instead, most Al_2Si_2Yb particles were observed adjacent the Si phase (Fig. 3), strongly indicating that most Yb atoms segregate out of eutectic Si.

5. CONCLUSION

(1) The solute adsorption of Sr atoms along the $<112>_{Si}$ growth direction of Si and at the intersection of Si twins during Si growth was observed, which can be used to interpret the well-known poisoning of the TPRE and IIT mechanisms, respectively.

(2) In contrast, the segregation of Yb atoms is distinctly different from the adsorption of Sr along the $\{111\}_{Si}$ growth planes. No significant Yb-rich cluster was observed at the intersection of Si twins.

(3) The solute entrainment of modifying elements (X) was proposed to interpret the formation of Al_2Si_2X (X, Sr or Yb) phase or X-rich clusters within eutectic Si. Such types of Al_2Si_2X phases or X-rich clusters were further proposed to be an "artefact" caused by the solute entrainment during eutectic Si growth, rather than a "true" modification mechanism.

(4) The proposed solute adsorption and entrainment can be used to well interpret the different observations in the cases of different modifying elements, thus elucidating the modification of eutectic Si in Al-Si alloys with respect to growth.

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