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Twin-controlled growth of eutectic Si in unmodified and Sr-modified Al–12.7%Si alloys investigated by SEM/EBSD



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ABSTRACT

The growth characteristics of eutectic Si in unmodified and Sr-modified Al-12.7%Si alloys were investigated by microstructure-correlated crystallographic analyses. For the unmodified alloys, the formation of repeated single-orientation twin variants enables rapid growth of eutectic Si according to the twin plane re-entrant edge (TPRE) mechanism. Microscopically, Si crystals are plate-like elongated in one (110) direction that is not in accordance with the (112) growth assumed by the TPRE model. The $\langle 110 \rangle$ growth direction is realized by paired $\langle 112 \rangle$ zigzag growth on parallel twinning planes, leading to alternate disappearance and creation of 141° re-entrants. As each twinning plane is associated with three re-entrants, Si crystals may extend in three co-planar (110) directions and cause the formation of equilateral plates. With the formation of α -Al around eutectic Si, the number of re-entrants is reduced. The planar isotropic growth of eutectic Si becomes anisotropic, leading to the formation of long plates. The reduction of the number of re-entrants also accounts for the width and thickness changes over the length of Si plates. This complex growth mode results in Si crystals exposing only their low-energy {111} planes to the melt. For the Sr-modified alloys, substantial changes appear in the eutectic Si morphology, attributable to the restricted TPRE growth and the impurity induced twinning (IIT) growth. The former enhances lateral growth by forming new twins with parallel twinning planes, while the latter leads to isotropic growth by forming differently oriented twins.

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1. Introduction

Al–Si alloys are the most widely used aluminum casting alloys owing to their superior castability (*e.g.* high fluidity), light weight, low thermal expansion coefficient, excellent thermal conductivity, high wear resistance and good corrosion resistance [1–3]. Among this alloy family, the eutectic Al–Si alloy – a typical non-facet/facet eutectic system – has been a subject of intensive studies. Basically, the microstructures of irregular Al–Si eutectics consist of coarse Si plates embedded in soft α -Al matrix. With trace additions of certain chemical modifiers, like Na and Sr [4–6], the eutectic Si phase is refined from coarse plate–like to fine fibrous

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structure. Such a morphological change – induced by chemical modification – is of industrial importance, because it improves the mechanical properties (*e.g.* strength and ductility) of Al–Si alloys.

To reveal the solidification patterns of irregular Al–Si eutectics, interest has long been focused on how the eutectic Si phase nucleates and grows. There are two widely accepted mechanisms explaining the growth behavior of eutectic Si in unmodified Al-Si alloys, namely layer growth [7] and twin plane re-entrant edge (TPRE) growth [8–10]. Layer growth postulates that a crystal surface consists of flat regions (terraces) and raised partial layers (steps), where atoms attach preferentially to the kink sites of steps. Since various crystal facets differ in growth rate [11], Si crystals would grow in an anisotropic manner. TPRE growth, on the other hand, says that the intersection of $\{111\}$ twinning planes with the outer surfaces of a Si crystal produces re-entrant corners, acting as favorable sites for atoms to stick and to make the crystal grow. Under such a mechanism, Si crystals grow preferentially in $\langle 112 \rangle$ directions [9,12].



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The chemical modification of eutectic Si crystals in Al-Si alloys may be associated with different mechanisms [1,13–19]. Regarding the Si nucleation, an addition of Sr or Na modifier is considered to reduce the potential AIP nucleation sites in Al-Si melt by forming Sr₃P/Na₃P [20,21] or Al₂Si₂Sr [22], which causes the eutectic Si nucleation at large undercooling. Concerning the Si growth, the impurity induced twinning (IIT) mechanism [16] based on the layer growth model and the restricted TPRE growth mechanism [12], are both well accepted. The former mechanism assumes that the adsorption of impurity atoms at monolayer steps on the solidliquid interface contributes to the alteration of the Si-{111} atomic stacking sequence and thus the formation of Si twins, thereby locally enabling isotropic growth in several Si-(112) directions. The latter mechanism assumes that chemical modifiers poison Si re-entrant grooves, thereby deactivating anisotropic TPRE growth. To verify possible modification mechanisms, detailed investigations on modifier distributions have been performed using high-resolution characterization techniques [17,23], such as three-dimensional atom probe tomography (APT) and transmission electron microscopy (TEM) [1,24,25]. A recent study by high-resolution TEM and atomic-resolution scanning electron microscopy (SEM) [26] revealed that Sr atoms are adsorbed along the (112) growth directions of Si crystals and/or at the intersections of multiple Si twins, thus evidencing an important role of the Sr modifier in the IIT growth and the restricted TPRE growth.

Although the TPRE growth and layer growth mechanisms are widely adopted to interpret the eutectic Si formation, the way in which the Si growth passes from the atomic scale to the microscopic scale have not been clearly addressed. Moreover, two requirements for the TPRE growth in unmodified Al-Si alloys, i.e. the $\langle 112 \rangle$ directional growth of eutectic Si and the exposure of Si-{111} planes to the melt to reduce interfacial energy, cannot be simultaneously satisfied. Such a situation arises from the lack of thorough investigation into the eutectic growth by correlated microstructural and crystallographic analyses at microscopic scale. In this regard, the SEM-based electron backscatter diffraction (EBSD) is a useful tool that bridges the thermodynamic measurements at macroscopic level and the advanced APT and high-resolution TEM examinations at nano and atomic scale. However, conventional EBSD systems suffer from a difficulty in differentiating the face-centered cubic α -Al phase (space group Fm3m, No. 225) and the diamond cubic Si phase (space group Fd3m, No. 227), as they generate very similar EBSD diffraction patterns. Therefore, special efforts must be made to separate the two eutectic phases without ambiguity.

In view of the above-mentioned open issues and the opportunity for a comprehensive analysis at microscopic scale, a thorough investigation on unmodified and Sr-modified eutectic Al–12.7Si alloys has been conducted in the present work. The SEM/EBSD system and a home-made dedicated post-analysis software package were used for the correlated microstructural and crystallographic analyses. The results are expected to provide some complementary information on the solidification behaviors of eutectic Al–Si alloys, especially the growth of eutectic Si.

2. Experimental details

The unmodified Al–12.7 (wt.%) Si alloy was prepared using pure Al (99.996 wt.%) and pure monocrystalline Si (99.999 wt.%) as raw materials. Bulk pure Al was melt in a 200 mL alumina crucible in an electric resistance furnace, and then pure monocrystalline Si was added to the pure Al melt after being held at 850 °C for 2 h. To obtain the modified Al–12.7Si alloy with 400 ppm Sr, an Al–10 (wt.%) Sr master alloy in required quantity was added into the Al–Si melt when the melt was cooled to 705 °C. Since the Sr

modifier is lost by oxidation during melting, the master alloy was produced by addition of excess Sr (13.7 wt.%) into the pure Al melt, followed by chill-casting into an iron mould. Prior to casting, the alumina crucibles and the iron mould were preheated at 200 °C for approximately 10 h to remove moisture and then cooled down to room temperature. Both the unmodified and Sr-modified Al–12.7Si alloys were slowly solidified in the 30 mL alumina crucibles, with a cooling rate not higher than 0.5 °C/s.

Specimens for microstructural observations and crystallographic analyses were taken from the middle of the as-cast ingots of the unmodified and Sr-modified Al-12.7Si alloys by wire-electrode cutting. Each specimen was mechanically ground with emery (SiC) papers up to $4000^{\#}$ (5 µm) and then polished with diamond suspension $(1 \mu m)$ to have a mirror-like sample surface. In order to remove the residual stress induced by the mechanical polishing, further polishing with oxide polishing suspension (OPS) was conducted on an automatic polishing machine at a rotation speed of 200-300 rpm for 10 min. The polished specimens were rinsed with tap water for 10 min and cleaned in ethanol in an ultrasonic bath for 30 min. To detect the three-dimensional (3D) morphology of the eutectic Si phase in the unmodified alloy, one polished specimen was subjected to electrolytic polishing to partially dissolve the α -Al matrix. The electrolytic polishing was performed using a solution of 20% perchloric acid in methanol at 25 V for 10 s at a temperature lower than 10 °C.

The microstructural observations were performed at room temperature using a JEOL JSM-6500F field emission gun SEM and a Zeiss Supra 40 field emission gun SEM. The crystallographic orientations of both eutectic α -Al and eutectic Si were analyzed with the JEOL SEM equipped with an EBSD camera and the Aztec acquisition software package (Oxford Instruments). The EBSD patterns were acquired at the acceleration voltage of 20 kV with two measurement step sizes (0.2 µm and 0.3 µm). The face-centered cubic (FCC) structure (space group Fm3m, No. 225) and the diamond cubic structure (space group Fd3m, No. 227) were utilized to index the Al and Si phases, respectively. The detailed crystal structure data are given in Table 1.

In the present work, two special efforts were dedicated to separating the eutectic α -Al and eutectic Si phases that could not be differentiated by conventional EBSD systems. Firstly, a preliminary separation was performed by choosing the "configuring groups of phases" option incorporated in the Aztec online acquisition software. Under this option, the band width information was used to distinguish the two phases automatically. Secondly, the complete phase differentiation was achieved using a home-made software, "Analysis Tools for Orientation Mapping (ATOM)" [27]. With the fully differentiated EBSD orientations of the two phases, further crystallographic information, including twin relationship and orientation preference (texture) of Si crystals, as well as orientation correlation between Si crystals and α -Al matrix, was derived using the Channel 5 data processing software package (Oxford Instruments). Possible orientation relationships (OR) between eutectic Si and α -Al were examined in conjunction with the published ones [20,28–32], where an allowable angular deviation of 5° was set to the specified plane and direction parallelisms.

To specify the growth direction and outer surface of Si crystals, the length vectors and surface trace vectors measured in the

Table 1
Crystal structure data used for identification of Al and Si phases by SEM/EBSD.

Formula	Structure	Atomic positions	Lattice parameters (Å)	Space group	No.
Al	FCC	4a	4.05	Fm3m	225
Si	Diamond	8a	5.4309	Fd3m	227

macroscopic sample coordinate system were transformed into the crystal coordinate system. This was readily done via coordinate transformation between two coordinate systems using the determined EBSD orientation data. Moreover, the representative length direction and surface plane, assessed on a statistical basis, were chosen as the extension direction and outer surface of eutectic Si crystals.

3. Results

3.1. Differentiation of eutectic α -Al and Si phases

For illustration, the secondary electron images (SEIs), EBSD phase-indexed micrographs and EBSD orientation micrographs of the unmodified and Sr-modified Al–12.7Si alloys are presented in Fig. 1. It can be seen that the eutectic α -Al and Si phases were fully differentiated without ambiguity. Apparently, the two phases

revealed in the EBSD phase-index micrographs (Figs. $1a_2$ and b_2) correspond well to their counterparts displayed in the SEIs (Figs. $1a_1$ and b_1). This validates the reliability of the above-mentioned phase identification procedure, thus allowing us to provide reliable information for both microstructural and crystallographic analyses.

3.2. Microstructural features of eutectic Si phase

Figs. 1a₃ and b₃ demonstrate that the microstructures of the unmodified and Sr-modified Al–12.7Si alloys consist of eutectic colonies, *i.e.* eutectic Si crystals are embedded in the continuous eutectic α -Al matrix. In order to reveal the 3D morphology of the unmodified eutectic Si phase, the secondary electron imaging was performed through capturing simultaneously two perpendicular sample sections (Fig. 2a), where the α -Al matrix was partially dissolved via electrolytic polishing. Generally, unmodified eutectic



Fig. 1. Microstructures of unmodified (upper) and Sr-modified (lower) Al–12.7Si alloys. (a_1) and (b_1) SEIs of eutectic phases (α -Al is in gray and Si in dark gray). (a_2) and (b_2) EBSD phase-index micrographs corresponding to (a_1) and (b_1) , respectively (α -Al is in blue and Si in red). (a_3) and (b_3) EBSD orientation micrographs with color code shown in the lower left corner of (a_3) . The step size of EBSD measurements is 0.3 μ m. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. (a) SEI plan view of unmodified eutectic Si crystals exposed in two perpendicular sample sections. The intersection of two perpendicular sample sections is marked with the red line, and one eutectic Si plate is outlined with the yellow lines. (b) Illustration of the distribution of multiple twins in one eutectic Si plate. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Si crystals have a long plate shape (as outlined in yellow in Fig. 2a) with irregular changes in width and thickness over the plate length direction. Within one eutectic colony, individual Si plates appear to be aligned in roughly the same direction with similar crystallographic orientation or twin-related orientation. The distribution of twins contained in one Si plate is schematically illustrated in Fig. 2b. Moreover, unmodified eutectic Si crystals seem to grow from the colony interior to exterior (as marked with A in Fig. 1a₃) and eventually grow past the colony boundary. This suggests that the unmodified eutectic Si grows into the Al–Si melt ahead of the α -Al phase, giving rise to the formation of non-smooth colony boundaries.

With the Sr addition, eutectic Si crystals become significantly refined from long plates to fine bars or particles (Fig. $1b_1$). In this case, the eutectic Si growth is constrained, no longer growing past eutectic colony boundaries. Clearly, the Sr modification has brought about a remarkable change in the formation of eutectic Si from anisotropic growth to nearly isotropic growth.

3.3. Extension direction and surface plane of eutectic Si crystals

Detailed calculations show that the length directions and outer surfaces of unmodified eutectic Si crystals correspond to their $\langle 110 \rangle$ directions and $\{111\}$ planes, respectively. This suggests that unmodified eutectic Si crystals are predominantly elongated in one $\langle 110 \rangle$ direction and encased by $\{111\}$ planes. As an example, Fig. 3a presents the EBSD orientation micrograph of one eutectic colony taken from the unmodified Al–12.7Si alloy. Figs. 3b–d display the $\langle 110 \rangle$, $\{111\}$ and $\langle 112 \rangle$ pole figures (PFs) of one twinned eutectic Si crystal outlined with the white dashed rectangle in Fig. 3a, where the vector \vec{a} represents both the extension directions and outer surface trace direction of the twinned Si crystal. One can

see from Fig. 3b that the vector OA joining the origin (O) of the

 $\langle 110 \rangle$ pole figure and the common $\langle 110 \rangle$ pole (A) of the twinned crystal is parallel to \vec{a} . Thus, the growth direction of the eutectic Si corresponds to one $\langle 110 \rangle$ direction. Similarly seen from

Fig. 3c, the vector OB connecting the origin (O) of the {111} pole figure and the common {111} pole (B) of the twinned crystal is nearly perpendicular to \vec{a} . This indirectly confirms that the outer surfaces of the eutectic Si are {111} planes. However, in Fig. 3d, there appear no common (112) poles, indicating that the growth direction of the eutectic Si is not parallel to (112). This is contrary to the previous claim that unmodified eutectic Si grows parallel to (112) [10,12,33].

Notably, the outer surface planes of the twinned eutectic Si crystal (Fig. 3b) are near-parallel to the Si-{111} twinning planes. Moreover, the growth directions of the two twin-related variants (Fig. 3a) are the same and contained in the {111} twinning planes. This configuration enables a unidirectional growth of the twinned eutectic Si crystal. Close examination has revealed that the {111} twinning planes are parallel to the Si plate surfaces and each Si plate is encased by several pairs of parallel {111} planes. As for the Sr-modified Al-12.7Si alloy, no fixed Si extension direction is attainable in one eutectic colony because the modified eutectic Si crystals are considerably refined and differently oriented (Fig. 1b₃).

3.4. Twin characters of eutectic Si crystals

The EBSD orientation micrographs and magnified SEM backscatter electron (BSE) images of eutectic Si crystals in the unmodified and Sr-modified Al–12.7Si alloys are shown in Fig. 4. Notably, almost all of the eutectic Si crystals contain twins (Figs. 4a₁ and b₁). Detailed crystallographic analysis has confirmed that these Si twins are of the {111}(1 1 $\overline{2}$) reflection type, being consistent with the published results. For the unmodified alloy (Figs. 4a₁ and a₂), only one-orientation twin variants appear with



Fig. 3. (a) EBSD orientation micrograph of one selected eutectic colony from unmodified Al–12.7Si alloy. (b) $\langle 110 \rangle$, (c) $\{111\}$ and (d) $\langle 112 \rangle$ PFs of one twinned Si crystal outlined with the white dashed rectangle in (a). Note that \overrightarrow{OA} is parallel to \vec{a} and \overrightarrow{OB} is nearly perpendicular to \vec{a} (with an angular deviation of about 4°), where \vec{a} specifies the growth direction of the twinned Si crystal.



Fig. 4. Twin characters of eutectic Si crystals in unmodified (upper) and Sr-modified (lower) Al–12.7Si alloys. (a_1) and (b_1) EBSD orientation micrographs (α -Al matrix is in white). (a_2) BSE image of Si crystals and (b_2) BSE image showing stepped twin interface traces. (a_3) BSE image showing multiple twinning plane traces in one Si crystal. (b_3) BSE image showing repeated single-orientation twin variants and multi-orientation twin variants in one Si crystal. The unmodified Si crystals in (b_2) and (b_3) are outlined with the red dashed lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

long and straight surface trace running from one tip to the other. Such single-orientation variants are repeatedly distributed over the thickness of eutectic Si plates (Fig. 4a₃), exhibiting the multiple twin character required by the TPRE growth mechanism [9,10]. Clearly, the traces of the {111} multiple twinning planes from one twinned Si crystal are parallel to each other, as illustrated in Fig. 2b. Thus, the multiple twinning does not change the extension direction of eutectic Si crystals.

As for the Sr-modified alloy, the modified eutectic Si twins (Fig. 4b₁) are different in two ways from those observed in the unmodified alloys. One is that twin interface boundaries are often not straight but curved or stepped, as shown in Fig. 4b₂. The other is that in many eutectic Si crystals both repeated single-orientation variants and multi-orientation variants appear, as shown in Figs. 4b₁ and b₃. Further crystallographic analysis indicates that the frequently occurring misorientation between multi-orientation twin variants is about 38.94° around $\langle 110 \rangle$. Certainly, the formation of multi-orientation Si twins should bring about a shape change of modified eutectic Si crystals, provided that the twin-controlled TPRE growth mechanism is effective.

3.5. Orientation preference of eutectic Si crystals

Fig. 5 presents the EBSD orientation micrographs of one eutectic colony taken from the unmodified and Sr-modified Al–12.7Si alloys, as well as the corresponding $\langle 110\rangle$ PFs of the Si crystals. In the unmodified case, eutectic Si crystals tend to be aligned locally in the same direction (Fig. 5a₁), where two adjacent Si crystals taks are correlated with a $\{111\}\langle 11\bar{2}\rangle$ twin relation. As shown in Fig. 5a₂, the twin-related eutectic Si crystals share three $\langle 110\rangle$ directions (circled in white) that lie in the twinning planes. One of the $\langle 110\rangle$ directions is the crystal growth direction (marked with A in Fig. 5a₂) shared by all Si crystals, which could be the heat flux direction during the solidification.

With the Sr addition, although the morphology of the eutectic Si crystals changes drastically (Fig. 5b₁), a $\langle 110 \rangle$ -type orientation preference can still be found in each eutectic colony (Fig. 5b₂). In

this case, most of the Si crystals share one single $\langle 1\,1\,0\rangle$ direction (circled with B in Fig. 5b₂), showing a tendency to form the $\langle 1\,1\,0\rangle$ fiber texture. This indicates that the growth habit of the unmodified eutectic Si is preserved for the Sr-modified eutectic Si to some extent.

3.6. Orientation relationship between eutectic α -Al and eutectic Si

In the literature, four types of direction parallelism between eutectic α -Al and eutectic Si are frequently reported, *i.e.* $\langle 0 \ 0 \ 1 \rangle_{Al} / / \langle 110 \rangle_{Si}$, $\langle 0 \ 0 \ 1 \rangle_{Al} / / \langle 0 \ 0 \ 1 \rangle_{Si}$, $\langle 112 \rangle_{Al} / / \langle 112 \rangle_{Si}$ and $(112)_{AI}/(110)_{SI}$ [20,28–32]. These direction parallelisms have been examined in the present work. For the unmodified Al-12.7Si alloy, there is no constant OR over the selected eutectic colonies, but very locally the $\langle 112 \rangle_{Al} / / \langle 112 \rangle_{Si}$ parallelism with some angular deviation (<5°) may occur, as shown as an example in Fig. 6a. For the Sr-modified Al-12.7Si alloy, the orientation correlation between the two phases becomes more random. Even in the same eutectic colony, several direction parallelisms exist, as shown in Fig. 6b. Therefore, under the present solidification conditions, no globally representative ORs can be identified for both unmodified and Sr-modified alloys. This indicates that the crystallographic compatibility across the phase interfaces is not the prerequisite for the formation of Al–Si eutectics. In other words, the formation of adjacent Si and α -Al couples does not require a specific OR (or ORs), but is rather random when the local composition of the melt is favorable for the formation of the two phases.

4. Discussion

4.1. Role of stacking fault in Si twinning

From the above observations on both unmodified and Sr-modified Al–12.7Si alloys, Si twins should be considered as an important microstructural constituent that is always linked with the growth process and the final morphology of Al–Si eutectics. To understand the crystallographic characters of the twins of the



Fig. 5. EBSD orientation micrographs of one eutectic colony and corresponding $\langle 110 \rangle$ PFs of eutectic Si crystals in unmodified (upper) and Sr-modified (lower) Al–12.7Si alloys. (a₁) and (b₁) EBSD orientation micrographs. (a₂) and (b₂) $\langle 110 \rangle$ PFs with coincident $\langle 110 \rangle$ poles circled in white.



Fig. 6. EBSD orientation micrographs of (a) unmodified and (b) Sr-modified Al–12.7Si alloys. Possible direction parallelisms between α-Al and adjacent Si are indicated, with a maximum allowable angular deviation of 5°.

eutectic Si phase, the atomic correspondence between twinned Si crystals is constructed with the specified $\{1\,1\,1\}\langle 1\,1\bar{2}\rangle$ relationship, as illustrated in Fig. 7. Clearly, Si twins cannot be easily generated by deformation, as a large amount of shear plus atomic shuffling would be required. However, they can be formed by faulted stacking during crystal growth, as Si possesses a relatively small stacking fault energy, about 50–60 mJ/m² [34].

For a perfect Si crystal, its diamond cubic structure consists of {111} close packed planes with a stacking sequence of ...AABBCCAA.... The formation of a twin would require faulted {111} layer, produced by either introducing one C atomic plane in the case of TP 1 or withdrawing one A atomic layer in the case

of TP 2 as shown in Fig. 7, plus a reversed stacking sequence ... AACCBBAA... with respect to the Si matrix. In both cases, only one atomic layer is necessarily faulted. Apparently, the reversed stacking sequence makes the twinned part unstable in the solidification environment. The original stacking sequence could be restored through introducing an additional stacking fault. This may be the reason why twinned parts of Si crystals are always thin and multiple twins occur very frequently in any given crystal.

Indeed, the formation of Si twins could be achieved by faulted deposition of atomic layers on the growth front (outer surfaces) of Si crystals [35]. During the crystallization of a eutectic Si crystal, its lowest-energy {111} planes are considered to be exposed to the



Fig. 7. Atomic correspondence between twinned crystals with diamond cubic structure, viewed on a (110) plane. Through (111) twinning planes (TP) marked with TP 1 and TP 2, the atomic stacking sequence ... AABBCCAA... of the matrix is changed to be ... AABBCCCBBAA... for TP 1 (inserting one C atomic layer) and ... CCBBABBCCAA... for TP 2 (withdrawing one A atomic layer), resulting in one 141° re-entrant and one 219° ridge, respectively.

melt. Under the thermo-solutal convection, stacking faults on the {111} planes can occur when Si atoms from the melt attach to the crystal, thus giving rise to the formation of twins. Molecular dynamic simulations on the growth of Si-Ge nanowires [35] have corroborated the formation of such stacking faults: four-atom Si clusters deposited at faulty locations on the Si-(111) facets, leading to the nucleation of twins. As Si crystals grow along the [111] direction layer-by-layer, this process would be repeated and then multiple parallel twins be formed.

4.2. Directional growth of unmodified eutectic Si

For the unmodified Al–12.7Si alloy, it is found that multiple eutectic Si twins are parallel to one another along the length direction of eutectic Si crystals (Fig. 4a₃). This is consistent with the condition required by the TPRE growth mechanism. The repeated single-orientation Si twins provide two (or more) parallel

{111} planes with a 141° re-entrant groove at the extension front for continuous growth, as illustrated in Fig. 7. The presence of a 141° re-entrant groove facilitates the preferential deposition of Si atoms in the melt along the $\langle 112 \rangle$ directions of the solidifying Si crystals. From Figs. 3b and c, it is clear that the growth direction of Si twins is in the {111} plane and the two twinned parts share the same growth direction. Under such a growth mechanism, eutectic Si crystals can grow efficiently in one or several $\langle 112 \rangle$ directions lying in the {111} twinning plane. However, the final growth direction of unmodified eutectic Si crystals is parallel to $\langle 110 \rangle$ (Fig. 3), rather than $\langle 112 \rangle$. Thus, the Si growth direction at the atomic scale is not the same as at the microscopic scale.

To find the reason for the above-mentioned discrepancy in Si growth direction, a 3D model illustrating one Si crystal with two parallel twinning planes (TP 1 and TP 2), is presented in Fig. 8. As the eutectic Si is commonly observed to expose its {111} facets to the melt to lower interfacial energy, the Si crystal depicted in



Fig. 8. Illustrations of a Si crystal with two parallel twinning planes TP 1 and TP 2. (a) Original configuration of two 141° re-entrants between planes 2 and 3 and between planes 4 and 5, and two 219° ridges between planes 1 and 4 and between planes 3 and 6. (b) Alternate disappearance and creation of 141° re-entrants across TP 1 and TP 2 to realize the (110) extension. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 8 is totally enveloped with {111} planes. At the growth front (colored in red in Fig. 8a), the intersection of one twinning plane with the outer {111} planes creates one 141° re-entrant groove and one 219° ridge. Taking the case of TP 1 as an example, the 141° re-entrant groove forms between planes 2 and 3, and the 219° ridge between planes 1 and 4 (Fig. 8a). Such re-entrant grooves enable the Si crystal to grow along one of the (112) directions in the respective twinning planes, *i.e.* $[11\overline{2}]$ in TP 1 and $[\overline{1}2\overline{1}]$ in TP 2. With the continuous deposition of Si atoms in the re-entrant grooves, the original {111} facets 1-6 (colored in red in Fig. 8a) evolve into $1^{*}-6^{*}$ (colored in pink in Fig. 8b). During this process, the initial 141° re-entrants are replaced by 219° ridges and vice versa. The growth in the $[11\overline{2}]$ direction in TP 1 (one 141° re-entrant between planes 2 and 3) and that in $[\bar{1}2\bar{1}]$ direction in TP 2 (one 141° re-entrant between planes 4 and 5) would result in the disappearance of these re-entrants and hence, the termination of further growth in these directions. However, two new 141° re-entrants, one between planes 1* and 4* associated with TP 1 and the other between planes 3* and 6* with TP 2, are created, as shown in Fig. 8b.

Although the disappearance of one re-entrant gives rise to the formation of a new re-entrant in the same direction, the Si growth front is shifted in one (110) direction and the extension pathway becomes zigzag. As illustrated in Fig. 9, the $[11\overline{2}]$ growth is interrupted by a shift in the $[\bar{1}01]$ direction and the $[\bar{1}2\bar{1}]$ growth by a shift in the $[1\bar{1}0]$ direction, each leading to an extension in the same $[01\overline{1}]$ direction. With such a scheme, the formed Si crystal (with parallel single-orientation twin variants) exposes only its {111} planes to the melt. This growth mode is advantageous in terms of interfacial energy, especially for slow-cooling solidification with low undercooling as in the present case. To sustain a continuous growth, at least two parallel twinning planes are required. Such a condition is demonstrated by the present experimental results, i.e. each Si crystal contains more than two twins and their surface traces run from one tip of the crystal to the other. As the growth of unmodified eutectic Si is anisotropic and that of eutectic α -Al is isotropic, eutectic Si crystals grow faster than α -Al matrix in the Si-(110) extension direction during the eutectic solidification. Thus, the eutectic Si phase could grow past eutectic colony boundaries, as frequently observed in the present unmodified Al-12.7Si alloy.

If the whole growth process of eutectic Si follows exactly the above proposed growth manner, Si crystals should adopt a bar shape. This seems to be conflict with the present observation that unmodified eutectic Si crystals are plate shaped. Indeed, the formation of plate-like crystals is also twin-controlled and realized via the TPRE mechanism. Fig. 10 illustrates one twinned Si nucleus with the same twin configuration as in Fig. 8. On one {111} twinning plane (TP 1, colored in blue), there are three equivalent $\langle 112 \rangle$ directions, each being associated with one re-entrant groove. If these re-entrant grooves are all exposed to the melt, they can



Fig. 10. Illustration of a twinned Si nucleus with the same twin configuration as shown in Fig. 8. One {111} twinning plane (TP 1) is colored in blue. Three 141° reentrant grooves associated with three $\langle 112 \rangle$ directions on TP 1 and three 219° ridges are indicated. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

receive Si atoms to make the nucleus grow. Such a growth is considered to be planar and isotropic. Consequently, it gives rise to the formation of plates provided that the Si eutectic is the leading phase during the eutectic solidification.

When the eutectic α -Al phase forms simultaneously, the planar isotropic growth of eutectic Si phase should stop. Since no specific OR between eutectic Si and α -Al is detected in the present work, one can infer that the formation of eutectic α -Al is controlled by normal coupled growth, rather than crystallographic compatibility between the two eutectic phases. The Si growth fronts (i.e. the re-entrant grooves) would act as ideal sites for the α -Al nucleation, as around these sites Si atoms are largely consumed and Al atoms are enriched. The formation of eutectic α -Al will block re-entrant grooves on the Si surfaces from the melt and make them inactive. With a reduced number of re-entrant grooves, the {111} planar isotropic growth of Si crystals is replaced by (110) directional growth, which results in long plates. Due to the irregular steric hindrance of α -Al on Si crystals, the morphology of eutectic Si crystals could be very different, depending on local solidification environment such as compositional and thermal perturbations. This may account for the irregularly shaped eutectic Si plates observed in the present work.

4.3. Restricted growth of Sr-modified eutectic Si

With an addition of 400 ppm Sr to the Al–12.7Si alloy, the habit of eutectic Si growth with $\{111\}\langle 11\bar{2}\rangle$ twin formation and preferred $\langle 110 \rangle$ extension is still present to some extent. For instance,



Fig. 9. Projection of TP 1 and TP 2 in Fig. 7 on one (111) atomic plane, showing the $[01\overline{1}]$ extension of twinned Si crystal through a paired $\langle 112 \rangle$ zigzag growth. The growth directions of $[11\overline{2}]$ in TP 1 and $[\overline{1}2\overline{1}]$ in TP 2 are indicated with the black solid and dashed arrow lines, respectively.

multiple twin variants are often observed in eutectic Si crystals (Fig. 4b₃) and the Si- $\langle 110 \rangle$ orientation preference is preserved in individual eutectic colonies (Fig. 5b₂). The present result suggests that the morphology modification of eutectic Si crystals occurs at the growth stage, being realized through "poisoning" of twin re-entrants as proposed and verified recently by many investigations [1,18,24,25,36]. The Sr modifier can be considered to restrict further growth of eutectic Si crystals associated with the original {111} twinning planes, which is in accordance with the restricted TPRE growth mechanism [12].

According to our experimental observations, the Sr modification on the morphology of eutectic Si crystals could be achieved in two different ways. One way is to block the Si growth on one initial {111} twinning plane and force the formation of new twins with the same twin orientation, which shifts the Si growth to the other {111} twinning planes that are parallel to the original twinning plane. As a result, the twin interface trace becomes curved or stepped (Fig. $4b_2$) and the lateral growth is enhanced. The other way is to block the Si growth along the original direction and force the formation of twins with different orientations (Fig. 4b₃). This leads to a change in the growth direction and the appearance of multi-orientation variants. Clearly, both the shift and change of the growth direction would retard the preferred (110) elongation and bring about a refinement of Si crystals. In general, the shift of the growth direction shortens a Si crystal in the initial growth direction and increases its thickness in the lateral direction, whereas the change of the growth direction results in an isotropic growth and thus the formation of quasi equiaxed crystals. Due to the Sr-induced deceleration of the directional extension in Si front, the growth velocities of α -Al matrix and Si crystals in one eutectic colony become comparable. Hence, no eutectic Si crystal would grow past a colony boundary.

5. Summary

The growth characteristics of eutectic Si crystals in slowly solidified Al–12.7Si alloys with and without Sr-modification have been thoroughly investigated using the SEM-based EBSD technique. The differentiation of the eutectic Si and α -Al phases was performed with a home-made software ATOM, which represents a prerequisite for the correlated microstructural and crystallographic analyses of the eutectic microstructures at a large scale with statistical reliability. In both unmodified and Sr-modified cases, the eutectic Si growth was found to be coupled with the formation of $\{111\}(11\overline{2})$ twins by faulted stacking of $\{111\}$ planes.

Unmodified eutectic Si crystals are in general long and plate shaped with appearance of multiple single-orientation twin variants along the long direction. It was demonstrated that the eutectic Si growth in the TPRE manner results in Si growth along (110), other than $\langle 112 \rangle$ assumed by the model. The microscopic $\langle 01\bar{1} \rangle$ growth direction is realized by a paired $\langle 11\bar{2} \rangle$ zigzag growth at atomic scale. Such a paired $\langle 11\bar{2}\rangle$ zigzag growth leads to the disappearance of initial re-entrant grooves and the creation of new re-entrant grooves in the same $\langle 11\bar{2} \rangle$ direction, accompanied by a shift in the corresponding $\langle \bar{1}01 \rangle$ direction in the same twinning plane. Under this growth scenario, Si twins expose only their lowest-energy {111} planes to the melt. This is advantageous in term of liquid/solid interfacial energy, especially for slow solidification with low undercooling. Prior to the eutectic α -Al formation, three Si re-entrant grooves associated with one twinning plane are all active, hence the eutectic Si growth is isotropic in that plane. Eutectic α -Al forms preferentially at the re-entrant grooves that are growing and therefore have enriched Al concentration, which therefore reduces the number of re-entrants. Thus, the eutectic Si growth changes from planar isotropic to directional (anisotropic)

and the equilateral plates evolve to become long plates. The reduction of re-entrant grooves during the growth process accounts for the shape irregularity of the eutectic Si plates, *i.e.* the width and thickness changes over the plate length.

As for Sr-modified eutectic Si crystals, both repeated single-orientation twin variants and multi-orientation twin variants, as well as curved or stepped twin boundaries, are frequently observed. The changes in eutectic Si morphology were demonstrated to be mainly associated with the growth process, as a result of the restricted TPRE growth and the IIT growth. More specifically, the restricted TPRE growth is realized by the deactivation of the initial twins and the formation of new twins with the same orientation, which enhances lateral growth. The IIT growth is realized by forming new twins with different orientations, thus changing the initial anisotropic growth to isotropic growth. Overall, the resulting eutectic Si crystals are significantly refined by the Sr modification.

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