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Crystallographic orientation relationships between primary silicon and aluminium crystals

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Crystallographic orientation relationships between the primary silicon crystal and the aluminium crystal heterogeneously nucleated on the silicon surface in hypereutectic Al–Si alloys, were studied by the micro-focus X-ray diffraction analysis. The apparently random orientation relationships obtained by X-ray analysis have been classified into simple relationships by taking the twinning in the primary silicon crystals into consideration. The epitaxial relationships between silicon and aluminium crystals in untreated alloys, and that in sodium-treated alloys, are found to be distinctly different.

1. Introduction

Binary eutectic alloys are sometimes classified into two categories according to their solidified microstructures; namely regular and irregular eutectic systems [1]. Regular eutectic systems have been the subject of many studies of the growth kinetics [2-7] and the relationships between the crystallographic orientation [8-15] of two phases.

The Al–Si system, similar to the Fe–C system, has a complex eutectic structure and is usually classified as a typical irregular type of eutectic system. A precise experimental determination of the crystallographic orientation relationships between the silicon and aluminium crystals is difficult to perform due to the irregularities of the eutectic microstructure. Early work performed by Straumanis and Brakes [16] reported that there was no relationship between the two phases. However, the frequent observation of a "halo" of aluminium around the primary silicon particles suggests the possibility of an expitaxial relation existing between these phases.

The purpose of this paper is to determine the crystallographic orientation of primary silicon crystals and that of eutectic aluminium heterogeneously nucleated on the primary silicon using a modern technique, i.e. micro-focus X-ray diffraction. The determination of the crystallographic orientation relationships between silicon and aluminium crystals should clarify the problems related to the mechanism of solidification as encountered in industrial uses of this material.

2. Experimental

A master alloy containing about 16 wt% silicon was prepared using 99.99% pure aluminium and high purity silicon (99.999%). In each experimental run, 20 g alloy was placed in a high purity alumina crucible and remelted at 800° C in a vertical resistance furnace. The specimens were then solidified under cooling conditions of 20° C min^{-1}. As a result of this slow cooling, the primary silicon crystals grew to sizes as large as several hundred microns long, with a halo of the aluminium phase 30 μm or more thick. The sodium treatment was carried out by covering the melts with a mixture of NaF and NaCl.

Optical microscopic observation of the solidified structure and micro-focus X-ray analysis by the back-reflection Laue method for crystallographic orientation determination, were performed on the polished sections of the specimens. The diameter of the micro-focus X-ray beam (Cu target at 50 kV acceleration) was 50 μm, and the maximum time of exposure was about 3 h. Six sodium-treated specimens and five untreated specimens, each taken from separate charges, were analysed.

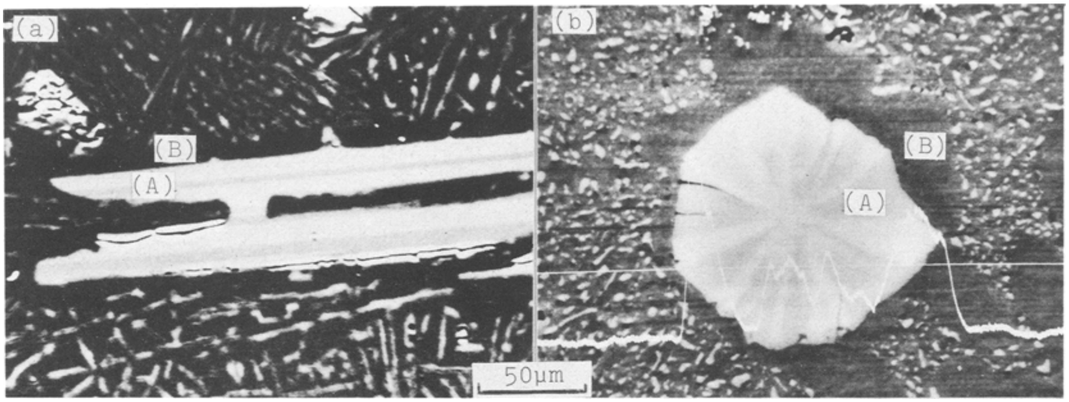


Figure 1 Back-scattered electron scanning images of slowly solidified Al–16 wt % Si alloys: (a) untreated; (b) sodium-treated. A and B indicate the positions in the specimens where the micro-X-ray Laue patterns were taken. Note the contrast in the primary silicon crystals due to multiple twinning.

3. Experimental results

The back-scattered electron scanning images of slowly solidified Al–16 wt % Si alloy are shown in Fig. 1. A and B indicate the position in the samples where the micro-X-ray Laue patterns were taken. After a standard process of orientation determination from these Laue patterns, no particular relations between the crystallographic orientation of primary silicon and that of the adjoining aluminium were recognized. This result seems to support the conclusion given by Straumanis and Brakes [16].

Recently, Kobayoshi *et al.* [17] studied the crystallographic growth habit of silicon crystal in untreated and sodium-treated Al–16 wt % Si melts and found that the crystals contain multiple twinning. A schematic drawing of a possible case of nucleation of an aluminium crystal on a twinned silicon crystal is shown in Fig. 2. When the aluminium "halo" is nucleated by the Si–(A) crystal, which is a twinned crystal of Si–(B), the apparent crystallographic relationship between the "halo" crystal and Si–(B) becomes complex and might be overlooked. Namely, in addition to the apparent crystallographic orientations obtained by X-ray diffraction, it is necessary to take into account the orientation of the silicon crystal twinned on one of the four $(1\,1\,\bar{1})$, $(1\,\bar{1}\,1)$, $(1\,1\,1)$ and $(1\,\bar{1}\,\bar{1})$ planes shown in Fig. 3, where those planes forming an octahedron are shown. Fig. 4 shows the rela-

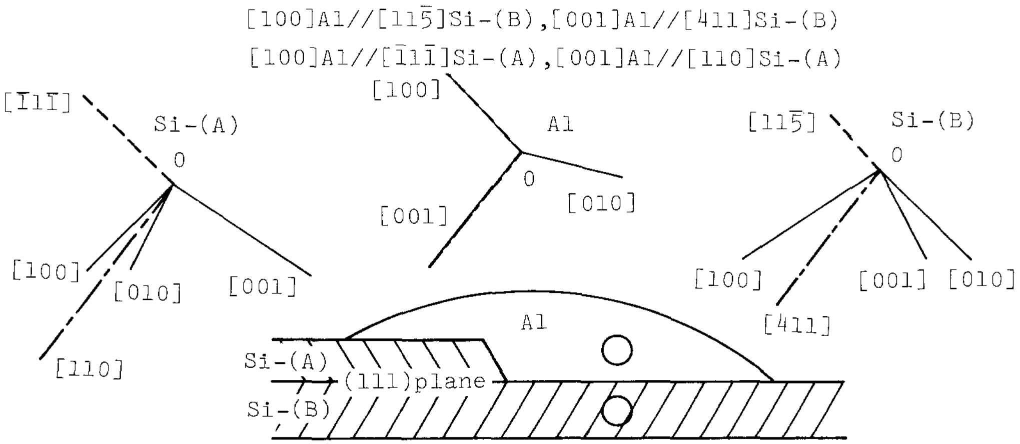


Figure 2 Schematic drawing of a possible case of nucleation of an aluminium crystal on a twinned silicon crystal. The circles indicate the area where the micro-focus X-ray diffraction pattern was obtained.
The crystallographic orientations for aluminium and Si–(B) crystals are determined from the diffraction pattern. The orientations for the Si–(A) crystal are obtained by applying the twinning operation to the orientations of Si–(B) crystal.

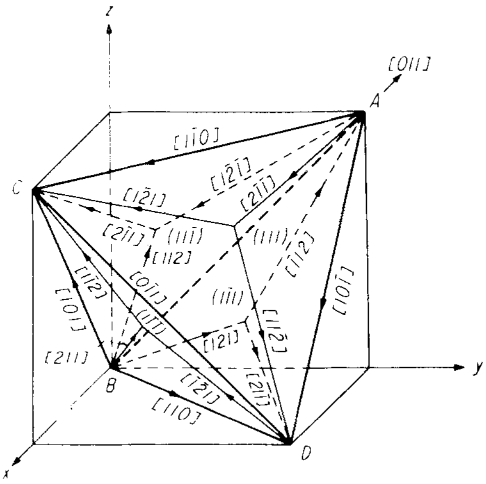


Figure 3 The four octahedral planes.

tionship between the original (1 0 0) standard projection and the projection after twinning on the $(1\,1\,\bar{1})$ plane.

Each Laue pattern from the silicon crystal was projected onto the diagram and compared with that obtained from the adjoining aluminium crystal. When the twinning in the primary silicon crystals is taken into consideration, untreated and sodium-treated specimens showed simple relationships as follows:

untreated

$$[0\,0\,1]\,\text{Ai}//[1\,1\,0]\,\text{Si},\quad [1\,0\,0]\,\text{Al}//[\bar{1}\,1\,\bar{1}]\,\text{Si} \qquad (1)$$

$$[0\,0\,1]\,\text{Al}//[1\,1\,0]\,\text{Si},\quad [1\,\bar{1}\,0]\,\text{Al}//[0\,0\,\bar{1}]\,\text{Si} \qquad (2)$$

$$[1\,\bar{1}\,0]\,\text{Al}//[0\,0\,\bar{1}]\,\text{Si},\quad [\bar{1}\,\bar{1}\,1]\,\text{Al}//[1\,0\,0]\,\text{Si} \qquad (3)$$

sodium treated

$$[0\,0\,1]\,\text{Al}//[1\,1\,0]\,\text{Si},\quad [0\,1\,0]\,\text{Al}//[\bar{1}\,1\,0]\,\text{Si} \qquad (4)$$

$$[0\,0\,1]\,\text{Al}//[1\,1\,0]\,\text{Si},\quad [1\,1\,0]\,\text{Al}//[\bar{1}\,1\,\bar{1}]\,\text{Si} \qquad (5)$$

$$[1\,1\,0]\,\text{Al}//[\bar{1}\,1\,\bar{1}]\,\text{Si},\quad [1\,\bar{1}\,1]\,\text{Al}//[1\,0\,\bar{1}]\,\text{Si}. \qquad (6)$$

Typical stereographic projections showing orientation relationships between silicon and aluminium crystals in untreated Al–Si alloys and in sodium-treated ones are shown in Figs. 5 and 6 respectively.

The mutual orientation relation between any pair of relations 1 to 6 may be expressed by the angle of rotation about a single rotation axis. Calculation of the rotation angle will be explained using the relationships 1 and 3 as follows: The orthogonal transformation matrix (T_{ij}) which

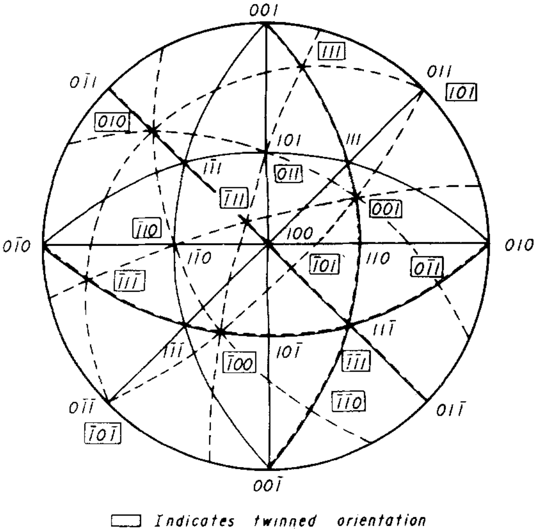


Figure 4 Relationship between the original (1 0 0) standard projection and the projection after the twinning operation on $(1\,1\,\bar{1})$ plane.

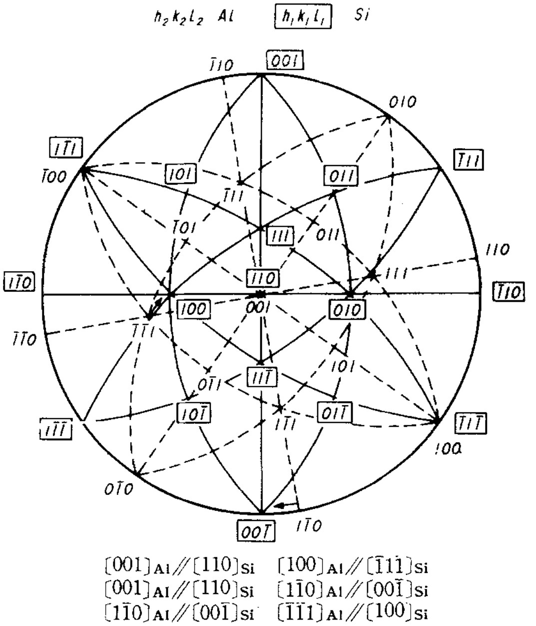
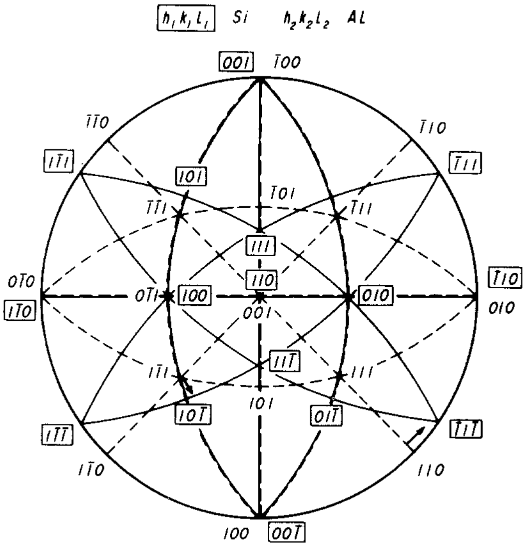


Figure 5 Typical stereographic projection showing orientation relationships between silicon and aluminium crystals of an untreated Al–Si alloy.



$[001]_{Al}//[110]_{Si}$ $[010]_{Al}//[\bar{1}10]_{Si}$
$[001]_{Al}//[\bar{1}10]_{Si}$ $[110]_{Al}//[\bar{1}1\bar{1}]_{Si}$
$[110]_{Al}//[\bar{1}11]_{Si}$ $[1\bar{1}1]_{Al}//[10\bar{1}]_{Si}$

Figure 6 Typical stereographic projection showing orientation relationships between silicon and aluminium crystals of a sodium-treated Al–Si alloy.

relates the lattice vectors of silicon and aluminium crystals in relation 1 is expressed as,

$$\begin{pmatrix}0\\0\\1\end{pmatrix}_{\mathrm{Al(1)}} = \frac{1}{\sqrt{2}}(T_{ij})\begin{pmatrix}1\\1\\0\end{pmatrix}_{\mathrm{Si}},$$

$$\begin{pmatrix}1\\0\\0\end{pmatrix}_{\mathrm{Al(1)}} = \frac{1}{\sqrt{3}}(T_{ij})\begin{pmatrix}\bar{1}\\1\\\bar{1}\end{pmatrix}_{\mathrm{Si}}. \qquad (7)$$

This transformation matrix (T_{ij}) is applied to the lattice vectors which express the orientation of the silicon crystal given in relation 3, to give the corresponding lattice vectors for the aluminium crystal,

$$\begin{pmatrix}e_1\\f_1\\g_1\end{pmatrix}_{\mathrm{Al(1)}} = (T_{ij})\begin{pmatrix}0\\0\\\bar{1}\end{pmatrix}_{\mathrm{Si}}, \quad \begin{pmatrix}e_2\\f_2\\g_2\end{pmatrix} = (T_{ij})\begin{pmatrix}1\\0\\0\end{pmatrix}_{\mathrm{Si}}. \qquad (8)$$

The relation between the above lattice vectors and the lattice vectors for the aluminium crystal given in relation 3 may be matched by another orthogonal transformation matrix (R_{ij}),

$$\begin{pmatrix}e_1\\f_1\\g_1\end{pmatrix}_{\mathrm{Al(1)}} = \frac{1}{\sqrt{2}}(R_{ij})\begin{pmatrix}1\\\bar{1}\\0\end{pmatrix}_{\mathrm{Al(3)}},$$

$$\begin{pmatrix}e_2\\f_2\\g_2\end{pmatrix}_{\mathrm{Al(1)}} = \frac{1}{\sqrt{3}}(R_{ij})\begin{pmatrix}\bar{1}\\\bar{1}\\1\end{pmatrix}_{\mathrm{Al(3)}} \qquad (9)$$

The above transformation matrix (R_{ij}) is expressed by a vector which expresses the rotation axis $[a\,b\,c]$ and the rotation angle θ as follows,

$$(R_{ij}) = \begin{pmatrix} a^2(1-\cos\theta)+\cos\theta,\, ab(1-\cos\theta)- \\ c\sin\theta,\, ac(1-\cos\theta)+b\sin\theta \\ ab(1-\cos\theta)+c\sin\theta,\, b^2(1-\cos\theta)+ \\ \cos\theta,\, bc(1-\cos\theta)-a\sin\theta \\ ca(1-\cos\theta)-b\sin\theta,\, bc(1-\cos\theta)+ \\ a\sin\theta,\, c^2(1-\cos\theta)+\cos\theta \end{pmatrix} \qquad (10)$$

and a, b and c may be solved from relation 9.

The calculated rotation angle between the relations 1 and 3 by the method described above was 13.8°, whereas that between the relations 1 and 2 was 9.7°. It was found that orientation relations 1 to 3 differ from each other by only a small amount and can be matched by a tilt of less than 13.8°.

The calculated rotation angle between relations 4 and 6 was 11.4° and that between relations 4 and 5 was 9.7°. Orientation relations 4 to 6 can again be matched by a tilt of less than 11.4°.

The calculated rotation angle between the two groups of orientation relations (untreated and sodium-treated) ranged from 44.9° to 54.7° indicating that the relations between silicon and aluminium crystals for untreated and sodium-treated cases are distinctly different. The observation of orientation relations 1 to 3 in the untreated specimens and 4 to 6 in the sodium-treated specimens suggests the existence of independent orientation relations with small orientation differences, although the possibility remains that the results for each group of specimens represent scatter from one orientation relation.

The orientation relationship between silicon and aluminium crystals, during solidification, is different from that in splat-cooled specimens [18], and also that between the aluminium matrix and precipitated silicon in aged specimens [19-22].

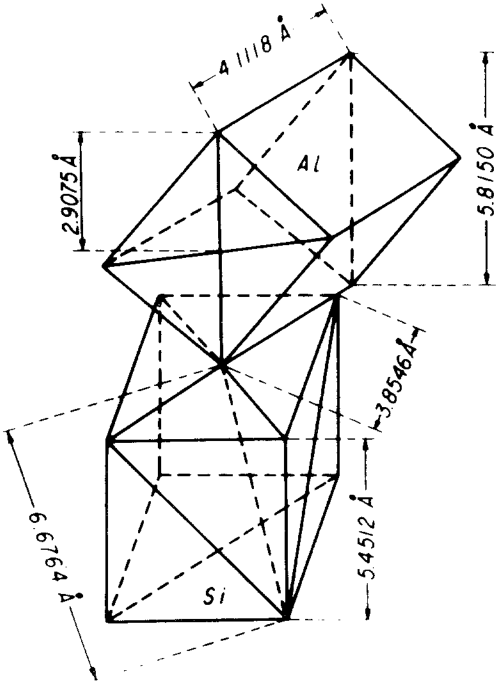


Figure 7 Schematic drawing showing orientation relationship between a primary silicon crystal and the aluminium halo in the sodium–treated Al–16 wt% Si alloy represented by relation 4. The atomic distances at 577° C (eutectic perature of this system) of both silicon and aluminium crystals shown in the figure are calculated by taking into consideration the liner expansion ratio and the solubility.

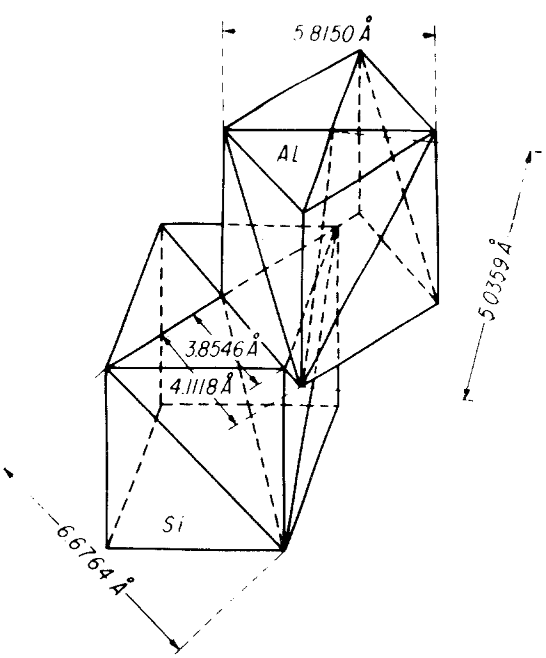


Figure 8 Schematic drawing showing orientation relationship between a primary silicon crystal and the aluminium halo in the sodium-treated Al–16 wt % Si alloy represented by relation 4. The atomic distances at 577° C (eutectic temperature of this system) of both silicon and aluminium crystals shown in the figure are calculated as given for Fig. 7.

4. Discussion

The crystallographic relationship between silicon and aluminium crystals in the untreated Al–Si alloy may be represented by the relation 1 as shown schematically in Fig. 7. Relations 2 and 3 can be matched to this relation by a slight rotation operation (less than 13.7° as stated in the previous section). The relationship between silicon and aluminium crystals in the sodium-treated alloy represented by relation 4 is shown in Fig. 8. Again, relations 4 and 5 can be matched to this relation by a rotation of 11.4°.

The origin of these two distinctly different epitaxial relationships may be explained by the

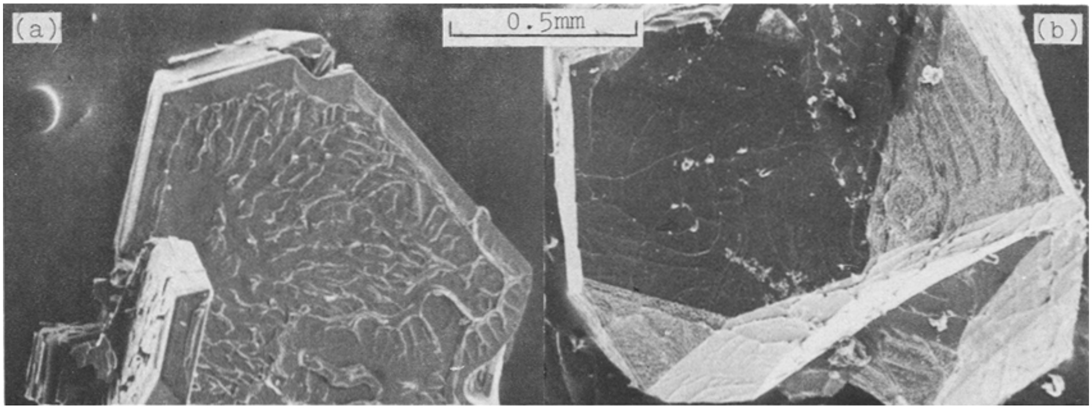


***Figure** 9* **Scanning electron micrographs of extracted primary silicon crystals of Al–16 wt % Si alloys: (a) untreated** silicon crystal, (b) sodium-treated silicon crystal.

difference in habit planes of primary silicon crystals in untreated and sodium-treated Al–Si alloys. The habit planes of primary silicon crystals in untreated and sodium-treated alloys are, as described in detail in previous work [17], markedly different. The primary silicon crystals in untreated Al–Si alloys grow as hexagonal plates whereas in sodium-treated alloys the crystals grow as granules, as shown in Fig. 9a and b. The habit plane in the untreated case is almost exclusively (1 1 1) which is the consequence of the re-entrant twin mechanism of crystal growth. On the other hand, habit planes other than (1 1 1) are frequently observed in the sodium-treated case.

The values of surface energy of Al–Si alloy are listed in Table I. The nucleation of aluminium crystals would take place on the less densely packed high free-energy crystal planes of silicon. When sodium-treated, (1 0 0) and other planes would be preffered to the (1 1 1) plane. However, in the case of untreated alloys, no plane is available for nucleation except the (1 1 1) plane.

TABLE I Surface energy values of an Al–Si alloy

Material	Value (erg cm^{-2})	References
Al (1 0 0)	1909	[23]
Al (1 0 0)	2017	[24]
Al (1 1 1)	1648	[23]
Al (1 1 1)	1747	[24]
Si (1 0 0)	1540	[24]
Si (1 1 1)	1240	[25]
Si (1 1 1)	1334	[24]
Untreated Al–Si eutectic solution	860	[26]
Sodium-treated Al–Si eutectic solution	670	[26]

These differences in the substrate silicon crystal planes of untreated and sodium-treated Al–Si alloys, should be the key to the different crystallographic orientation relationships between silicon and aluminium crystals. When the indices of the substrate crystal plane are fixed, the method of orientation on the substrate of the nucleating phase may be determined by the periodicity of the atom arrangement of the two phases on the matching plane, and the chemical interaction energies between atoms on the plane, to give the observed specific relationships between silicon and aluminium crystals.

5. Conclusion

Crystallographic orientation relationships between primary silicon and aluminium crystals heterogeneously nucleated on the silicon surface in hypereutectic Al–Si alloys, were studied by microfocus X-ray diffraction analysis. The apparently random orientation relationships obtained by X-ray analysis have been classified into simple relationships when the twinning in the primary silicon crystals is taken into consideration. These relationships are;

$$[0\,0\,1]\,\mathrm{Al}//[1\,1\,0]\,\mathrm{Si},\quad [1\,0\,0]\,\mathrm{Al}//[\bar{1}\,1\,\bar{1}]\,\mathrm{Si} \tag{1}$$

$$[0\,0\,1]\,\mathrm{Al}//[1\,1\,0]\,\mathrm{Si},\quad [1\,\bar{1}\,0]\,\mathrm{Al}//[0\,0\,\bar{1}]\,\mathrm{Si} \tag{2}$$

$$[1\,\bar{1}\,0]\,\mathrm{Al}//[0\,0\,\bar{1}]\,\mathrm{Si},\quad [\bar{1}\,\bar{1}\,1]\,\mathrm{Al}//[1\,0\,0]\,\mathrm{Si} \tag{3}$$

for untreated alloys and,

$$[0\,0\,1]\,\mathrm{Al}//[1\,1\,0]\,\mathrm{Si},\quad [0\,1\,0]\,\mathrm{Al}//[\bar{1}\,1\,0]\,\mathrm{Si} \tag{4}$$

$$[0\,0\,1]\,\mathrm{Al}//[1\,1\,0]\,\mathrm{Si},\quad [1\,1\,0]\,\mathrm{Al}//[\bar{1}\,1\,\bar{1}]\,\mathrm{Si} \tag{5}$$

$$[1\,1\,0]\,\mathrm{Al}//[\bar{1}\,1\,\bar{1}]\,\mathrm{Si},\quad [1\,\bar{1}\,1]\,\mathrm{Al}//[1\,0\,\bar{1}]\,\mathrm{Si} \tag{6}$$

for sodium-treated-alloys.

The occurrence of relation 1 for untreated alloys and relation 4 for sodium-treated alloys are most frequent, and the two groups of three orientation relationships (1 to 3 and 4 to 6) can be matched to each other, within each group, by a tilt of less than 13.8° and 11.4° respectively. The calculated rotation angle between the two groups of the orientation relations (untreated and sodium-treated) was between 44.9° and 54.7°, indicating that the relationship between silicon and aluminium crystals for untreated and sodium-treated cases, are distinctly different.

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