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Differences of grain-refining effect of Sc and Ti additions in aluminum by empirical electron theory analysis

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Abstract: The differences of grain-refining effect between Sc and Ti additions in aluminum, which cannot be substantially explained by traditional theories, were carefully studied. The empirical electron theory (EET) of solids and molecules was employed to calculate the valence electron structures (VES) of Al_3Ti and Al_3Sc. The conclusions can be drawn that, in the two alloys Al-Ti and Al-Sc, the different valence electron structures of Al_3Ti and Al_3Sc and the consequent differences of growth habit of the two particles, and the different interfacial electron density between particles and matrix fundamentally lead to the differences of grain-refining effect between Sc and Ti additions on aluminum and make Sr the better grain-refiner of aluminum.

Key words: grain refining; empirical electron theory (EET); valence electron structure (VES); Al_3Sc; Al_3Ti

1 Introduction

It has long been established that the formation of a fine scale, equiaxed grain structure is desirable in Al-castings because it can improve the mechanical properties, reduce hot tearing, increase feeding to eliminate shrinkage porosity, and give a more uniform distribution of second phases[1]. The usual method of controlling the cast grain structure of aluminum is the deliberate addition of master alloys containing melt inoculants, the most common of which is based on the Al-Ti system[2−3]. However, nowadays, researchers from different countries have paid much attention to scandium (Sc) additions in aluminum, which can perform a better grain-refining effect[4−8].

Ti and Sc, which are in the adjacent locations of periodic system of elements, are both effective refiners of aluminum and aluminum alloys. A large number of primary particles act as effective nucleation sites during the subsequent solidification[4, 9−10]. Much of the existing literature has demonstrated that Sc is so far found to be the most effective grain refiner of aluminum, which, however, to our knowledge, is simply attributed to the very low lattice misfit between the primary Al_3Sc particles and the Al matrix. In fact, it cannot be decided that either Sc or Ti has a better refining effect on aluminum just from the traditional theory: 1) Generally, peritectic reaction is preferred for a grain refiner, for it gives a clean interface of non-homogeneous nucleation sites. The reaction between the Al_3Sc and α(Al) phases is an eutectic one, while that between the Al_3Ti and α(Al) phases is a peritectic one[4, 9]. 2) Although the coherence between the $L1_2$ Al_3Sc and α(Al) is much better than that between the tetragonal DO_{22} Al_3Ti and α(Al)[11−12], which might lead to a better refining effect of Sc on aluminum than Ti, there is still another factor that definitely cannot be neglected, i.e., the number of nuclei in unit-volume melt. 3) By taking the solute concentration of 0.7% (mass fraction) as an example, the mass fraction of Al_3Ti in the melt will be 2.65 times higher than that of Al_3Sc[13]. Because the densities of Al_3Sc and Al_3Ti are close to each other (3.026 g/cm^3 and 3.37 g/cm^3), if the dimension of primary Al_3Sc particle is close to that of Al_3Ti, then the number of Al_3Ti particles will be much larger than that of Al_3Sc, which may offset the influence of the second factor.

It cannot be decided that either Ti or Sc is better for grain-refinement of aluminum with these three factors

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above. In the present work, experiments have been curried out to study the different grain-refining effects of Sc and Ti additions on aluminum, and the valence electron structures (VES) have been calculated, using the empirical electron theory (EET) of solids and molecules, which can help to achieve a deeper understanding of this interesting phenomenon.

2 Experimental

The different-composition alloys used in this work were prepared using pure aluminum (99.99%), Al-2.12Sc and Al-2.15Ti (%, mass fraction) master alloys. The cylindrical cast samples were produced by pouring the molten alloys with a 50 K superheat into a mould. A sample was taken from each casting and ICP-AES (inductively coupled plasma atomic emission spectroscopy) was employed to determine the final composition. These results are displayed in Table 1 and demonstrate that the actual compositions are very close to the nominal compositions.

Table 1 Nominal alloy compositions and analysis results (mass fraction, %)

Al-Ti alloy No.	Nominal content of Ti	Analysis content of Ti	Al-Sc alloy No.	Nominal content of Sc	Analysis content of Sc
1	0.05	0.05	1	0.05	0.05
2	0.1	0.11	2	0.1	0.12
3	0.2	0.20	3	0.2	0.19
4	0.4	0.38	4	0.4	0.41
5	0.5	0.49	5	0.5	0.48
6	0.7	0.71	6	0.7	0.68
7	0.9	0.93	7	0.9	0.91
8	1.2	1.22	8	1.2	1.23

To observe the grain-refining effect with naked eyes, the samples were etched using enriched Keller's reagent after mechanical polishing. To reveal the grain structure for optical metallography, the samples were electropolished in the mixture of perchloric acid and acetic acid, and subsequently anodized in Baker's reagent and examined under polarized light. For scanning electron microscope (SEM) examination, samples were lightly electropolished and examined to achieve backscatter electronic images in a FEI Quanta 200 FEG, operated at 15 kV. EDS was employed to determine the composition of different phases.

When a grain size of less than 500 μm was observed, the mean linear intercept method was used to measure the average grain size[14]. However, for the samples with very large grain (of the order of millimeters), the grain size was estimated directly from the samples.

3 Results and analysis

3.1 Experimental results

Fig.1 shows the naked-eye observation of the different refining effects of Sc and Ti additions on aluminum. The grain sizes of Al-Ti and Al-Sc against the Sc or Ti content are displayed in Fig.2. When the solute content is low ($<$0.6%, mass fraction), Ti has a better refining effect on aluminum than Sc, and an unrefined large grain size is measured in Al-Sc alloy. When the content of Sc is increased beyond a certain value (around 0.5%), a dramatic reduction in the grain size is observed in Al-Sc, thus Sc performs a much stronger refining effect on aluminum than Ti when the contents of Sc and Ti are larger than 0.7%.

Fig.3 presents metallographic images of the grain structures of Al-Ti and Al-Sc alloys. Equiaxed grains with an average size of 220 μm are achieved in Al-0.2Ti, while coarse columnar grains with the size order of millimetre still dominate in Al-0.2Sc. When the solute content is increased up to 1.2%, the grain size of Al-Ti alloy is around 90 μm without large difference compared with Al-0.2Ti. While for Al-1.2Sc, there is a total absence of dendritic sub-structure, the grain size is sharply decreased to around 25 μm.

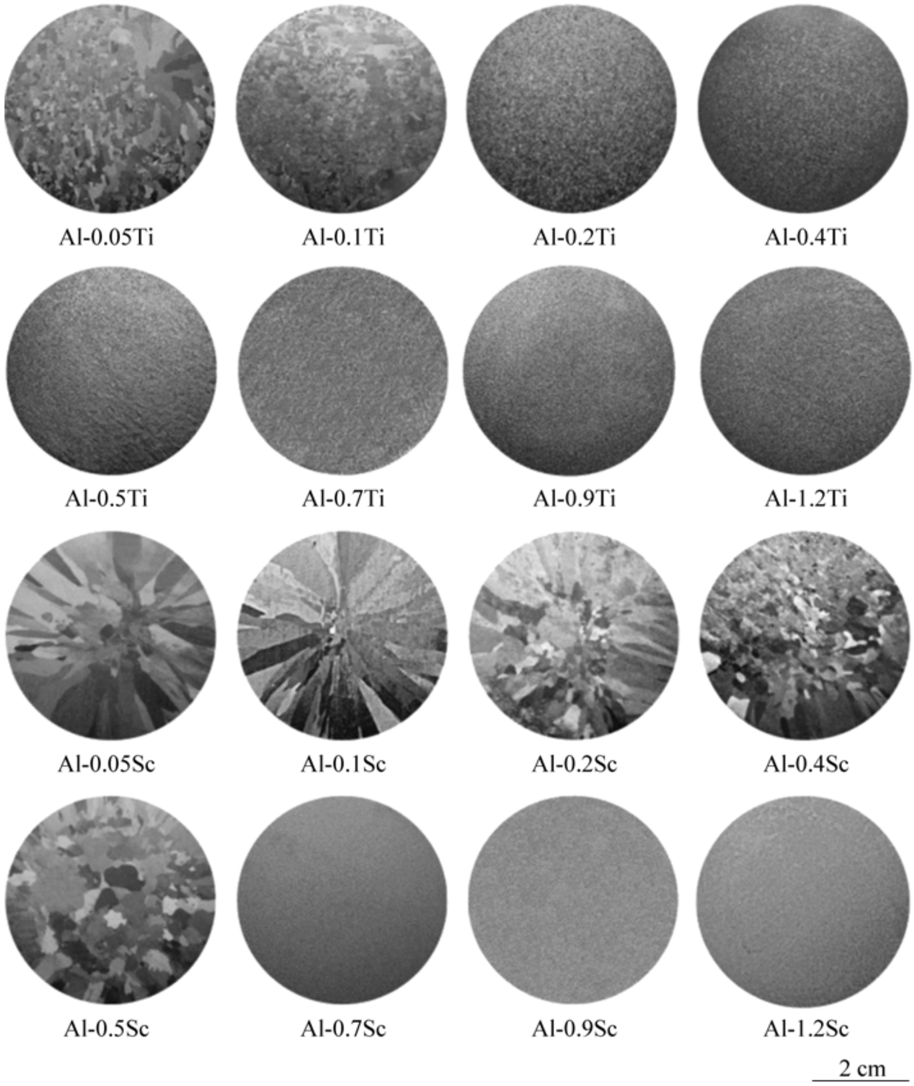
In the backscatter electronic images (Fig.4), it is obvious that Al_3Ti in Al-1.2Ti is needle-like in 2D, with a dimension of 80−120 μm, while Al_3Sc is cubic with a size of 5−10 μm.

3.2 EET analysis

3.2.1 EET explanation of numbers of Al_3Sc and Al_3Ti

The empirical electron theory (EET) of solids and molecules, founded by YU[15], gives a description of valence electron structure (VES) of crystal on the basis of atom state using an ingenious method[16−17]. As one of the most promising electron theories[18], EET has been recently employed by many researchers, achieving inspiring results[19−23]. VES of Al_3Sc and Al_3Ti has been calculated by EET[13], and the results are shown in Table 2, in which $D_{n\alpha}$ stands for a covalent bond length between two atoms, n_α for covalent electron pair number of the bond, and α for the sequence number of the bonds, marking as A, B, C, D, E, according to the length of bonds. It is necessary to indicate that, the hybrid level σ of Al in Al_3Sc is chosen to be 6 in Ref.[13], which is considered to be not appropriate in this work. The hybrid level σ_{Al} is chosen to be 5 here because it is more reasonable when it is not under extreme condition[24−25].

The n_α values of the strongest bond A and the second stronger bond B of Al_3Ti are higher than those of



Al-0.05Ti Al-0.1Ti Al-0.2Ti Al-0.4Ti

Al-0.5Ti Al-0.7Ti Al-0.9Ti Al-1.2Ti

Al-0.05Sc Al-0.1Sc Al-0.2Sc Al-0.4Sc

Al-0.5Sc Al-0.7Sc Al-0.9Sc Al-1.2Sc

Fig.1 Grain-refining effect comparison of Al-Ti and Al-Sc alloys with same solute content

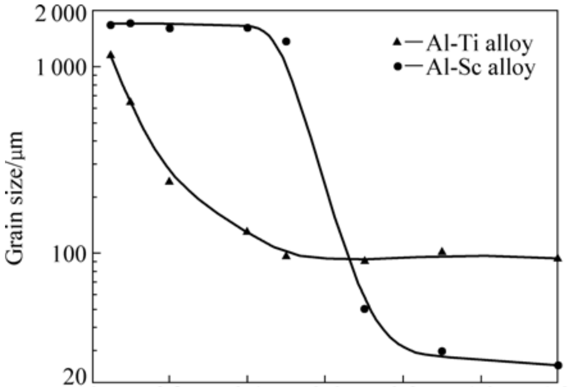


Fig.2 Plot of grain size vs solute content of Al-Ti and Al-Sc alloys

Al_3Sc, respectively (Table 2). Even the fourth stronger bond D of Al_3Ti has a higher n_α value than the second stronger bond of Al_3Sc. The strongest bond of α(Al) has a relative small n_α value of 0.208 6[26]. These indicate that there is a strongest tendency to combine Al and Ti, and Al_3Ti is easiest to precipitate during solidification, which is more difficult for Al_3Sc unless the content of Sc in Al-Sc alloy is increased beyond a certain value. Therefore, if a small quantity (e.g. 0.2%) of Ti and Sc are respectively added to Al, Al_3Ti tends to precipitate substantially, while Al_3Sc does not. This also qualitatively explains why the critical content for Al_3Sc to precipitate in Al-Sc is 0.55% (mass fraction) (0.33%, molar fraction), while for Al_3Ti in Al-Ti alloy, it is only 0.15% (mass fraction) (0.08%, molar fraction). However, if the content of added element is increased beyond a certain value (around 0.7%, mass fraction), for Al_3Ti there will be a more and more serious segregation. Although the quantity of Al_3Ti is much larger than Al_3Sc, excessive growth and serious reunion will lead to a smaller number of individual Al_3Ti particles than individual Al_3Sc particles, whose dimension is smaller because of the relatively low n_α values.

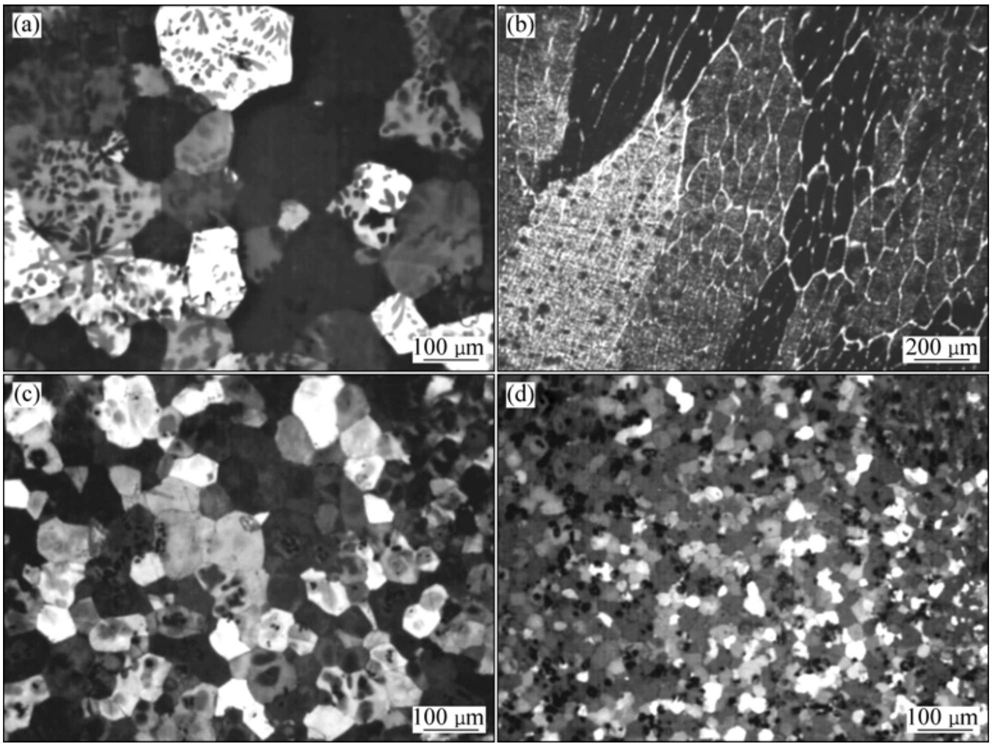


Fig.3 Grain structures of Al-Ti and Al-Sc alloys: (a) Al-0.2Ti; (b) Al-0.2Sc; (c) Al-1.2Ti; (d) Al-1.2Sc

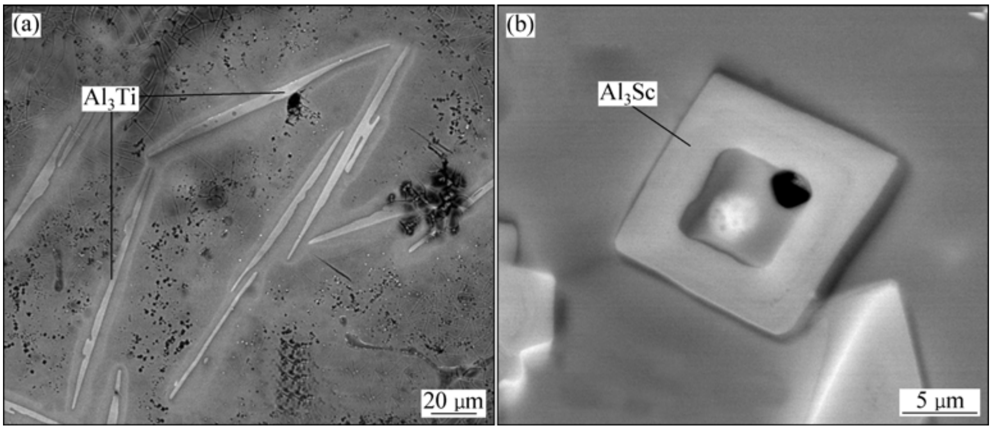


Fig.4 Backscattered electron images of primary Al_3Ti in Al-1.2Ti (a) and primary Al_3Sc in Al-1.2Sc (b)

Table 2 Valence electron structures of Al_3Sc and Al_3Ti[13]

Bond of Al_3Sc	Bond length/Å	n_α	Bond of Al_3Ti	Bond length/Å	n_α
A	$D_{n\alpha}^{Sc-Al}=2.903$	0.325 8	A	$D_{n\alpha}^{Ti-Al(2)}=2.723$	0.399 0
B	$D_{n\alpha}^{Al-Al}=2.903$	0.132 1	B	$D_{n\alpha}^{Al(1)-Al(1)}=2.723$	0.267 5
C	$D_{n\alpha}^{Sc-Sc}=4.105$	0.008 0	C	$D_{n\alpha}^{Ti-Al(1)}=2.888$	0.212 2
D	$D_{n\alpha}^{Al-Al}=4.105$	0.001 3	D	$D_{n\alpha}^{Al(1)-Al(2)}=2.888$	0.142 2
E	$D_{n\alpha}^{Sc-Al}=5.028$	0.000 1	E	$D_{n\alpha}^{Ti-Ti}=3.851$	0.007 8

For Al_3Sc, hybrid level $\sigma_{Al}=5$, $\sigma_{Sc}=6$; For Al_3Ti, $\sigma_{Al}=5$, $\sigma_{Ti}=9$.

3.2.2 EET explanation of crystallization efficiency of Al-Sc and Al-Ti alloys

In the DO_{22} Al_3Ti, the n_α values of bond A and bond B, which are located in the (001) crystal plane, are much higher than those of bond C and bond D, which are located in the (010) crystal plane (Fig. 5). Because of the stronger combining tendency of the atoms, the (001) crystal plane will extend more rapidly than the (010) crystal plane, which leads to anisotropy of the growth of Al_3Ti. Therefore, Al_3Ti grows to a needle-like shape in 2D (Fig.4), with a much larger dimension in the *x* and *y* directions than in the *z* direction (Fig.5), leaving only the (001) crystal plane facing the melt; and thus leads to a relatively low crystallization efficiency of Al matrix. Whereas, because of a high degree of symmetry of the atomic bonds in the $L1_2$ Al_3Sc (Fig.5), it grows to a cubic structure with more crystal planes facing the melt (Fig.4), offering more nucleation sites for α(Al).

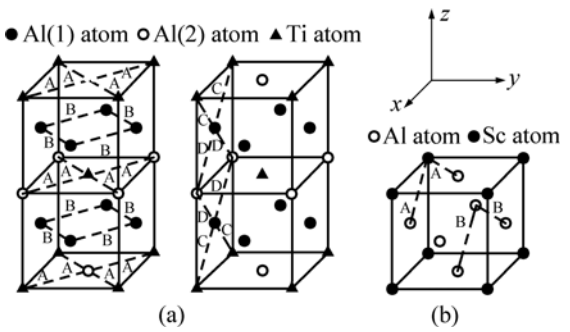


Fig.5 Diagrammatic sketches of crystal structures of Al_3Ti and Al_3Sc, and bonds with most valence electrons: (a) Al_3Ti; (b) Al_3Sc

Through calculation and analysis of electronic densities of two-phase interfaces in Al-Sc and Al-Ti alloys, the mechanism of grain refinement in the two alloys can be discussed further. There are following orientations on the two-phase interface in Al_3Sc:

$$\begin{cases}\{001\}_{Al_3Sc}//\{001\}_{Al}\\ \langle 110\rangle_{Al_3Sc}//\langle 110\rangle_{Al}\end{cases} \tag{1}$$

For the crystal plane (001) of Al_3Sc, there are

$$\begin{cases}D_A=2.903\ \text{Å}, n_A=0.325\,8, I_A=8\\ D_C=4.105\ \text{Å}, n_C=0.008\,2, I_C=4\\ D_D=4.105\ \text{Å}, n_D=0.001\,3, I_D=4\end{cases} \tag{2}$$

The total number of shared electrons on each covalent bond of this crystal plane is

$$\sum n_c^{(001)}=n_A I_A+n_C I_C+n_D I_D=2.644 \tag{3}$$

The area of the crystal plane is

$$S_{(001)}^{Al_3Sc}=a^2=16.851\ \text{Å}^2 \tag{4}$$

Covalent bond electron density of this crystal plane is

$$\rho_1=\frac{2.644}{16.851}=0.157\ \text{Å}^{-2} \tag{5}$$

Similarly, the covalent bond electron density of the (001) crystal plane of α(Al) can be calculated:

$$\begin{cases}D_A=2.864\ \text{Å}, n_A=0.208\,6, I_A=4\\ D_B=4.410\ \text{Å}, n_B=0.004\,4, I_B=4\end{cases} \tag{6}$$

$$\sum n_c^{(001)}=n_A I_A+n_B I_B=0.852 \tag{7}$$

$$S_{(001)}^{Al}=a^2=16.4\ \text{Å}^2 \tag{8}$$

$$\rho_2=\frac{0.852}{16.4}=0.052\ \text{Å}^{-2} \tag{9}$$

The difference of electron densities is

$$\Delta\rho_{(Al_3Sc\text{-}Al)}=\frac{|\rho_1-\rho_2|}{\frac{1}{2}(\rho_1+\rho_2)}=100\% \tag{10}$$

There are following orientations on the two-phase interface in Al_3Ti:

$$\begin{cases}\{001\}_{Al_3Ti}//\{001\}_{Al}\\ \langle 110\rangle_{Al_3Ti}//\langle 110\rangle_{Al}\end{cases} \tag{11}$$

For the (001) crystal plane of Al_3Ti, there are

$$\begin{cases}D_A=2.723\ \text{Å}, n_A=0.399\,0, I_A=8\\ D_E=3.851\ \text{Å}, n_E=0.007\,8, I_E=4\\ D_F=3.851\ \text{Å}, n_F=0.003\,5, I_F=4\end{cases} \tag{12}$$

$$\sum n_c^{(001)}=n_A I_A+n_E I_E+n_F I_F=3.237 \tag{13}$$

$$S_{(001)}^{Al_3Ti}=14.822\ 5\ \text{Å}^2 \tag{14}$$

$$\rho_1=\frac{3.237}{14.8225}=0.218\ \text{Å}^{-2} \tag{15}$$

The difference of electron densities is

$$\Delta\rho_{(Al_3Ti\text{-}Al)}=\frac{|\rho_1-\rho_2|}{\frac{1}{2}(\rho_1+\rho_2)}=123\% \tag{16}$$

The interfacial electron density difference on the interface $(001)_{Al_3Sc}//(001)_{Al}$, 100%, is smaller than that on $(001)_{Al_3Ti}//(001)_{Al}$, 123%, which means the electron density is more continuous on the interface $(001)_{Al_3Sc}//(001)_{Al}$ than on $(001)_{Al_3Ti}//(001)_{Al}$, as shown in Fig.6. Thus, the interfacial stress and the interfacial energy between Al_3Sc and α(Al) is smaller than that between Al_3Ti and α(Al). Consequently, Al_3Sc offers a better nucleation sites for α(Al) with a higher efficiency of crystallization than Al_3Ti.

4 Conclusions

1) The higher n_α (covalent electron number of a bond) values of bonds of Al_3Ti than Al_3Sc lead to a

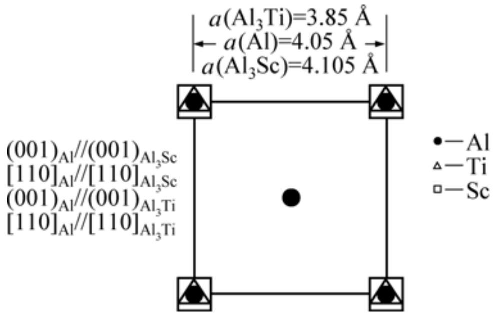


Fig.6 Schematic diagram of relation in interface $(001)_{\mathrm{Al_3Sc}}//(001)_{\mathrm{Al}}$ and $(001)_{\mathrm{Al_3Ti}}//(001)_{\mathrm{Al}}$

stronger precipitation and reunion tendency of Al_3Ti than Al_3Sc, and thus a smaller number of individual Al_3Ti particles than individual Al_3Sc particles when the solute content is beyond a certain value.

2) The different n_α values between bonds in different crystal planes of Al_3Ti lead to anisotropy of the growth of Al_3Ti, which grows to needle-like shape in two-dimension, leaving only the (001) crystal plane facing the melt. However, Al_3Sc with a high degree of symmetry of atomic bonds, grows to a cubic structure with more crystal planes facing the melt, offering more nucleation sites for α(Al). Besides, the more continuous electron density at the interface in Al_3Sc offers better nucleation sites for α(Al). Therefore, the crystallization efficiency of Al-Sc alloy is relatively high.

3) With a larger quantity of particles and higher crystallization efficiency, Sc is proofed a better grain-refiner of aluminum than Ti.

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