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Aluminum matrix composite reinforced by in-situ formed intermetallic Al_3Ti ①

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[Abstract] The reinforced phase of in-situ formed intermetallic compound Al_3Ti with grain size about 0.5 μm in the aluminum matrix composite was achieved by the method of liquid-solid reaction under specific condition. The orientations were also studied. The results show that under T6 heat treatment regime, the tensile strength, hardness, elastic modulus and elongation of Al_3Ti/ZL101 in-situ composite are increased by 32.8%, 14.4%, 19.2% and 14.6% respectively in comparison with those of ZL101. Al_3Ti is uniformly distributed in α(Al) matrix with a clear phase interface, and the orientation relationship between Al_3Ti and α(Al) is $(006)_{Al_3Ti} // (0\bar{2}2)_{Al}$, $[\bar{1}22]_{Al_3Ti} // [1\bar{1}0]_{Al}$. The strengthening mechanisms of Al_3Ti/ZL101 in-situ composite is proved to be caused by fine grain size, spreading distribution and dislocation multiplication.

[Key words] in-situ composite; microstructure; mechanical properties; reinforcement mechanism
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1 INTRODUCTION

The study of aluminum matrix composite is focused on the method of adding reinforcing phase such as sintering, spraying and liquid stirring. These processing methods not only have complex fabrication technology and high cost but also have poor bonding between matrix and reinforcing phase[1, 2]. A new method to form the composite by in-situ chemical reaction has been developed in these years[3]. In this study, the intermetallic compound Al_3Ti is selected as the reinforcing phase. Al_3Ti/ZL101 in situ composite is manufactured by liquid-solid reaction method. The morphology and distribution of reinforcing phase, strengthening mechanism, mechanical properties and microstructure of this in-situ composite are studied systematically.

2 SELECTION OF REINFORCING PHASE AND FORMATION THERMODYNAMICS OF Al_3Ti

It is confirmed by the theory of local density function (LDF) that the structure of Al_3Ti can be transformed from DO_{22} to $L1_2$ through the addition of alloying elements and can be stabilized resulting from the formation of cubic pseudo binary alloy. Al_3Ti with $L1_2$ structure is suitable to be chosen as a reinforcing phase for strengthening Al matrix. Following reaction will take place by adding TiO_2 to melting aluminum alloy:

$$13Al(l) + 3TiO_2(s) = 3Al_3Ti(s) + 2Al_2O_3(s) \tag{1}$$

Gibbs energy difference of this reaction at any temperature will be expressed as follows[4, 5]:

$$\Delta G_T = \Delta G^{\ominus}_{(298\,K)} + \int_{298\,K}^{T} \sum_B c_p \, dT + \int_{298\,K}^{T} \frac{\sum_B \upsilon_B c_p \, dT}{T}$$
$$= -749\,584.37 + 34.836\ln T + 40.011 \times 10^{-3} T - 71.21 \times 10^5 T^{-2} + 10.81 \times 10^{-3} T^2 - 57.606 \times 10^5 T^{-1} \tag{2}$$

The ΔG calculated from above equation at certain temperature are as follows:

$\Delta G(1\,053\,K) = -743.75\ (kJ \cdot mol^{-1})$;
$\Delta G(1\,273\,K) = -736.76\ (kJ \cdot mol^{-1})$;
$\Delta G(1\,373\,K) = -734.06\ (kJ \cdot mol^{-1})$

It can be seen from these results that ΔG of forming Al_3Ti by in-situ reaction is about −743.75 kJ/mol and in-situ reaction has very high growing tendency, but this reaction speed is very low at normal process. When the reaction temperature is in the range of 1 000～1 100 ℃, ΔG of Eqn.(1) will be −736.76 ～ −734.06 $kJ \cdot mol^{-1}$. Thermodynamics drive is very great at this temperature range and the activity of the reaction will be greatly advanced. Therefore the in-situ reaction can be finished instantly. Adding Na_3AlF_6 can generate following change:

$$2TiO_2 + 2Na_3AlF_6 = 2Na_2TiF_6 + Na_2O + Al_2O_3 \tag{3}$$

$$Na_2TiF_6 + 3Al = 2NaF + 2F_2 + 2Al_3Ti \tag{4}$$

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NaF, Na_2O and Al_2O_3 formed by reaction will be removed. The stirring force created by F_2 can make Eqns. (3) and (4) be fast.

3 EFFECT OF MANUFACTRUING PROCESS ON GRAIN SIZE AND MORPHOLOGY OF Al_3Ti

The size of reinforcing phase created by in-situ reaction is generally lower than 1.0 μm and this phase will distribute inside matrix at solidification. It has binding force because Al_3Ti has the same crystal structure as aluminum matrix. The reinforcing phase will destroy the continuity of matrix and affect the mechanical properties of composite.

3.1 Producing method

Three producing methods are used to form Al_3Ti reinforced composite:

1) After melted, pure aluminum is heated to 1000~1100 ℃ under covering of cryolite, then added with solid TiO_2. The chemical reaction will be taken place and intermetallic compound Al_3Ti and Al_3Ti/Al composite (noted as material A) will be produced.

2) The temperature of material A is decreased to 780 ℃, then added with 7% Si and 0.3% Mg respectively in order to obtain Al_3Ti/ZL101 in-situ composite (noted as material B).

3) The aluminum alloy matrix containing 7% Si and 0.3% Mg is heated to 1000~1100 ℃ under covering of cryolite, then added with solid TiO_2 in order to form Al_3Ti and Al_3Ti/ZL101 in-situ composite (noted as material C).

3.2 Microstructure of in-situ composite

Fig. 1 shows as-cast microstructure of material A. It can be seen that some long needle-like second phase distribute in α(Al) matrix. The length of this second phase is about 200~300 μm. The grain size of in-situ composite is very coarse.

Fig. 2 shows as-cast microstructure of material B. It can be seen that a number of needle-like eutectic Si distribute on α(Al) dendritical crystalline. The size of α(Al) grain is about 50 μm and the size of needle-like eutectic Si is about 20~40 μm. The rod-like phase in the microstructure is also the Al_3Ti phase and its size is about 80 μm.

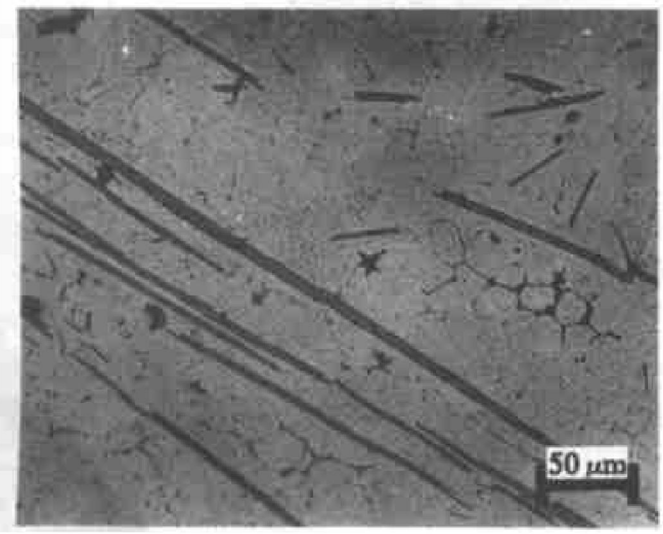

Fig. 1 Microstructure of material A

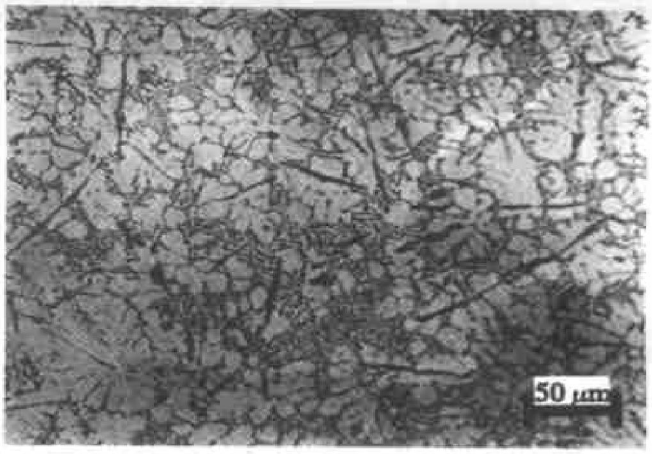

Fig. 2 Microstructure of material B

Fig. 3 shows as-cast microstructure of material C. This microstructure is consisted of α(Al) dendritical crystal and needle-like eutectic Si. The size of α(Al) crystal and eutectic Si is about 40 μm and 20 μm respectively. Al_3Ti phase is not visible at low magnification because it is very small. Comparing Fig. 3 with Fig. 2, it can be found that although these two composites have same chemical composition, the size of α(Al) crystal and eutectic Si in material C are much smaller than those in material B.

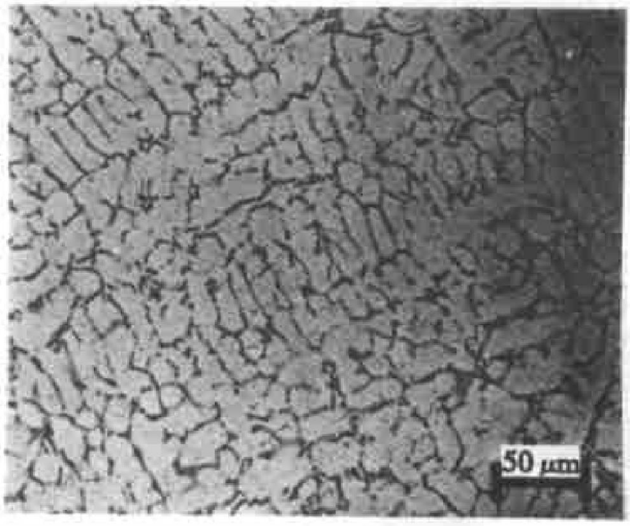

Fig. 3 Microstructure of material C

TEM observation for material C (as shown in Fig. 4) shows that the reinforcing phase is of rod-like form, it distributes inside the α(Al) dendritical crystalline uniformly and its size is about 0.5 μm. The results show that when adding element Si in material A, the size of needle-like Al_3Ti phase will be refined. In Al-Si-Ti system, Si will be combined with Al_3Ti to form ternary nonstoichiometric intermetallic compound $(Al_{1-x}Si_x)_3Ti$ ($x < 0.5$). The existence of Si has no effect on the crystal lattice parameter. The orientation relationship between Al and $(Al_{1-x}Si_x)_3Ti$ is as same as that between Al and Al_3Ti. Otherwise, in Al-Ti binary phase diagram, there is a peritectic reaction at 650 ℃, $L + Al_3Ti \rightarrow \alpha(Al)$. After reaction, a part of Al_3Ti formed in advance will be dissolved and transformed into $\alpha(Al)$. This reaction, therefore, will not only result in a part of Al_3Ti dissolved so that some Al_3Ti with long needle-like morphology will be broken down and turned into rod-like with smaller size, but also form a nucleus of crystal for the peritectic reaction. Thirdly, because of existing Si, Ti content of Al_3Ti phase in the front of growing will be decreased, and the growth of Al_3Ti along the needle direction will be restrained, the speed of growing, therefore, will be slowed down[6, 7].

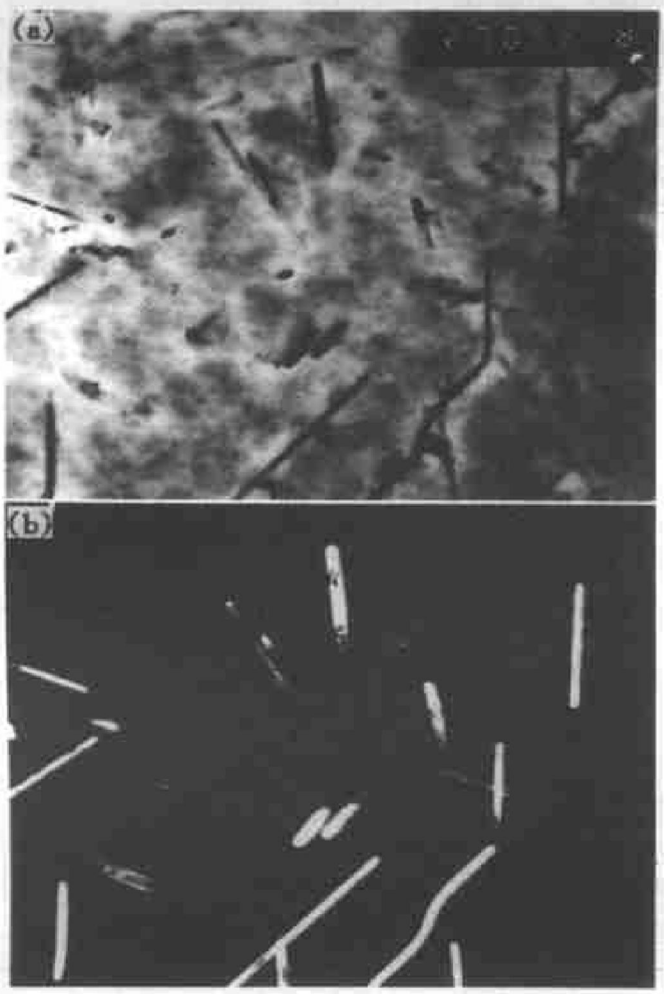

Fig. 4 TEM analysis of material C
(a) —Bright field; (b) —Dark field

The formation of Al_3Ti consists of the following procedures: 1) Generating Al_3Ti crystal nuclei because of the composition fluctuation. Since the inner energy of the alloying liquid at high temperature by mechanical stirring is increased, Ti content in some local region will be higher than the average Ti content so that the condition of generation Al_3Ti nuclei will be satisfied. 2) Al_3Ti growing because of diffusion. After nucleation, whether Al_3Ti nuclei grow or not depends on the growing speed of Al_3Ti nucleus and the Ti diffusion speed in the alloying liquid.

In the formation process of Al_3Ti/Al in-situ composite, the region close to Al_3Ti nucleus will become a layer of Ti deficiency after generating Al_3Ti nucleus. Since there is no resistance caused by other elements for Ti diffusion in $\alpha(Al)$, its diffusion speed will be very fast. Thus, Ti diffusion becomes the dynamica control factor and results in Al_3Ti growing to 200~ 300 μm. After 7% Si and 0.3% Mg are added, the adding Si will be interacted with Al_3Ti to form the ternary nonstoichiometric intermetallic compound $(Al_{1-x}Si_x)_3Ti$ ($x < 0.5$). At 650 ℃, the aluminum alloy containing Ti will have a peritectic reaction. Since both Si and Al_3Ti have joined the reaction, a small needle-like grain of $(Al_{1-x}Si_x)_3Ti$ with size about 80 μm will be resulted[5]. In the process of forming Al_3Ti/ZL101 in-situ composite, the region close to Al_3Ti nuclei will become a layer with Ti deficiency but rich Si after Al_3Ti nucleation. Since the speed of Ti diffusion is rapidly reduced because of the diffusion obstacle resulted from Si in the layer of Ti deficiency, growth of Al_3Ti nuclei, will be restricted further. Meanwhile, in alloy liquid Al_3Ti nuclei could be generated according to the following mechanism: 1) Al_3Ti nuclei generation caused by composition fluctuation; 2) the outer borderline of the layer with Ti deficiency but rich Si has a certain Ti content and relatively high Si content, which is easy to form nuclei of $(Al_{1-x}Si_x)_3Ti$. Since growth of Al_3Ti nuclei will be formed with very low growing speed, the final grain size of Al_3Ti will be remained to a level about 0.5 μm. 3) Adsorption effect of the solid in solution.

After reinforcing phase Al_3Ti is formed, its grain size is very small while the specific surface is very large, so, it will have an adsorption effect on the around medium. In solution, the adsorptive amount of solid solute can be agreed with the laws of Freundlich and Langmuir. As a result, the amount of Si around Al_3Ti will be increased. Furthermore the more amount of Al_3Ti, the more Si adsorption is.

Freundlich equation can be expressed as

$$\frac{x}{m} = kC_B^{1/n} \quad (5)$$

where x is the mole fraction of solute Si element, m is the mass of adsorptive agent Al_3Ti, C_B is the concentration of solute Si, and k and n are constant number. It can be seen from Eqn. (5) that solid Al_3Ti in melting alloy will adsorb solute Si. The more amount of Al_3Ti and Si, the more Si adsorption is.

Langmuir equation can be expressed as

$$\frac{x}{m} = \frac{bC_B}{1 + bC_B} \quad (6)$$

where b is a constant. It can be seen from this equation that solid Al_3Ti in melting alloy will adsorb solute Si[4,5]. The more amount of Al_3Ti and Si, the more Si adsorption is.

After forming Al_3Ti phase, the layer of outer borderline of Al_3Ti with Ti deficiency but rich Si is formed. The concentration of solute Si around Al_3Ti is higher than that of average amount. Since the speed of Ti diffusion is rapidly reduced and the adsorptive amount of Si growth, the final grain size of Al_3Ti will be remained to be about 0.5 μm.

3.3 Manufacturing process for Al_3Ti/ZL101 in-situ composite

The aluminum alloy matrix containing 7% Si and 0.3% Mg is heated to 1 000~ 1 100 ℃ under covering of cryolite, added with solid TiO_2 and reacted to form Al_3Ti phase, then, Al_3Ti/ZL101 in-situ composite will be obtained. Fig. 5 shows the X-ray diffraction spectrum of in-situ composite Al_3Ti/ZL101.

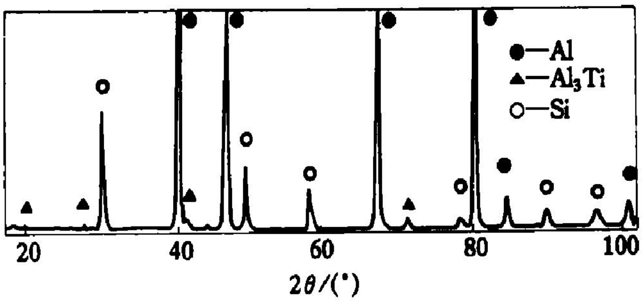

Fig. 5 X-ray spectrum of material C

4 MECHANICAL PROPERTIES OF Al_3Ti/ZL101 IN-SITU COMPOSITE

The mechanical properties of samples at room temperature after heat treatment are listed in Table 1. It can be seen that the tensile strength, hardness, elastic modulus and elongation of Al_3Ti/ZL101 in-situ composite are increased by 32.8%, 14.4%, 19.2%, 14.6% respectively in comparison with those of ZL101.

Table 1 Mechanical properties of samples after heat treatment

Material	σ_b/MPa	δ/%	HB	E/GPa
ZL101	262	4.1	98	77
Al_3Ti/ZL101	348	4.7	112	91

5 STRUCTURAL ANALYSIS OF REINFORCING PHASE Al_3Ti

Fig. 6 shows TEM diffraction pattern of Al_3Ti/ZL101 in-situ composite. It can be seen that reinforcing phase Al_3Ti is distributed inside α(Al) matrix uniformly and its size is about 0.3~ 0.5 μm. The interface binding between α(Al) matrix and Al_3Ti is very well, and has no any interface reaction. The orientation relationship between Al_3Ti and α(Al) matrix is $(006)_{Al_3Ti} // (0\bar{2}2)_{Al}$, $[\bar{1}22]_{Al_3Ti} // [1\bar{1}0]_{Al}$.

Fig. 7 shows the TEM morphology of Al_3Ti in Al_3Ti/ZL101 in-situ composite. A part of the rod-like Al_3Ti is inlaid inside α(Al) matrix, the other part of the rod is exposed outside. It can be seen from the interface between Al_3Ti and α(Al) matrix that the binding boundary is very clear. Indexing out TEM diffraction pattern of Al_3Ti/ZL101 in-situ composite, it is shown that the diffraction pattern is consisted of α(Al) and Al_3Ti.

Fig. 8 shows a TEM analysis images of Al_3Ti/ZL101 in-situ composite. It can be seen that the end of Al_3Ti has got very smooth transitional arc. After Al_3Ti phase with such a kind of morphology combined with the matrix, which can dramatically reduce the stress concentration between reinforcing phase and matrix, and improve the binding structure of interface, the aluminum alloy liquid forms Al_3Ti, because the richness of Si in the front of Al_3Ti and formation of aluminide containing Si slow down the growth speed of reinforcing phase greatly. In such case, growth with preferred orientation is easy to grow in coordination with the surrounding growth orientation, and form a smooth transitional arc in the front. Its diffraction pattern is of typically $L1_2$ superlattice, which indicates that Al_3Ti is an intermetallic compound with $L1_2$ structure.

6 STRENGTHENING MECHANISM

6.1 Fine grain strengthening

The strength of Al_3Ti/ZL101 in-situ composite depends on α(Al) grain size firstly. Hall-Petch equation expresses this contribution to strength of fine grain. Since Al_3Ti is the role of heterogeneous nucleus, the grain size of α(Al) in composities is much smaller than that of α(Al) in ZL101, which is resulting in remarkably strengthening for the matrix.

Reinforcing phase Al_3Ti formed in-situ can also have an effect on refining and spheroidizing of eutectic Si. Globular eutectic Si can reduce the continuous destruction of α(Al) matrix and play a role of strengthening. It can be seen from Fig. 6(b) and (d) that the eutectic Si grain size of ZL101 material is about 15 μm but the eutectic Si grain size of in situ composite is about 5 μm after heat treatment. The contribution of eutectic Si grain to strength is also expressed by Hall-Petch equation. Because fine eutectic Si grain distributes in α(Al) matrix, it can reduce the continuous destruction of α(Al) matrix and strengthen this composite.

The smaller the grain size of reinforcing phase, the more evident for the strengthening effect is. Since

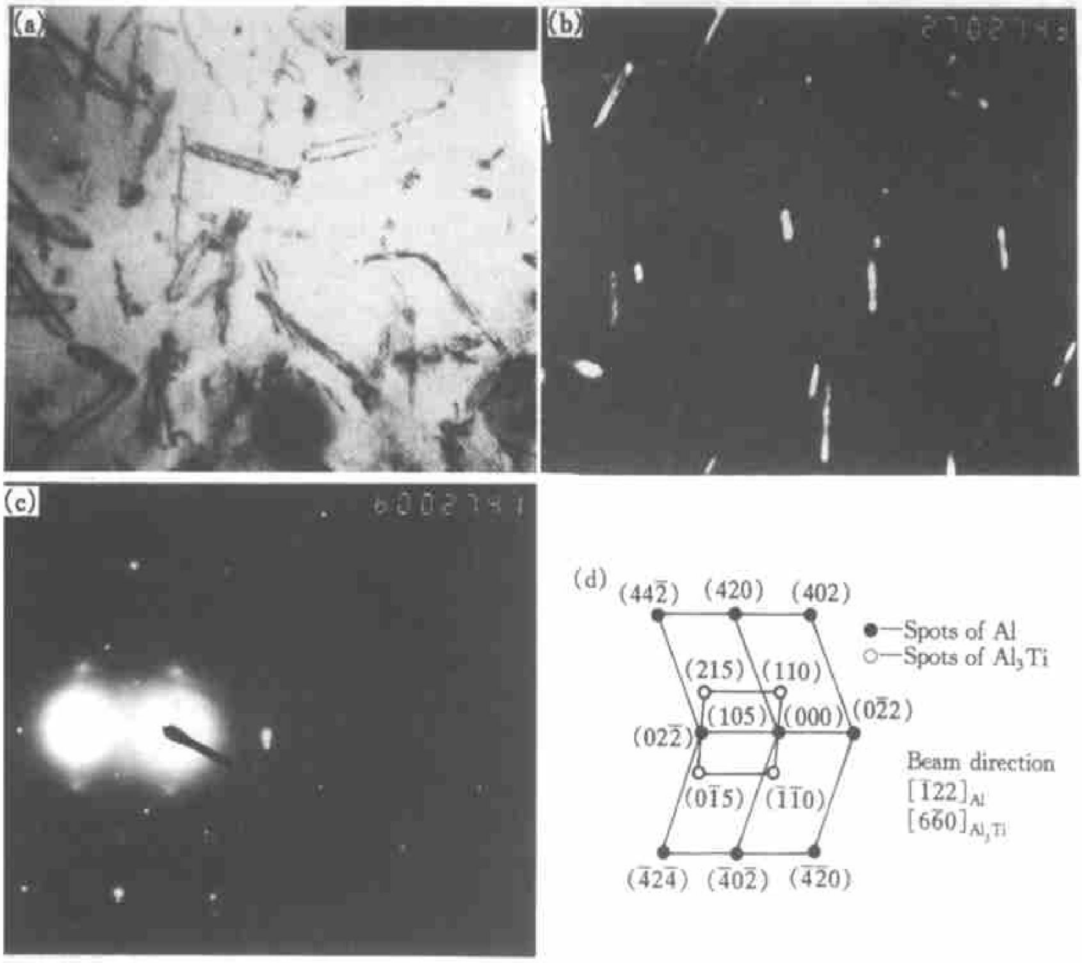

Fig. 6 TEM diffraction pattern of Al_3Ti/ZL101 in-situ composite

(a) —Bright field; (b) —Dark field; (c) —Diffraction pattern; (d) —Indexing diffraction pattern

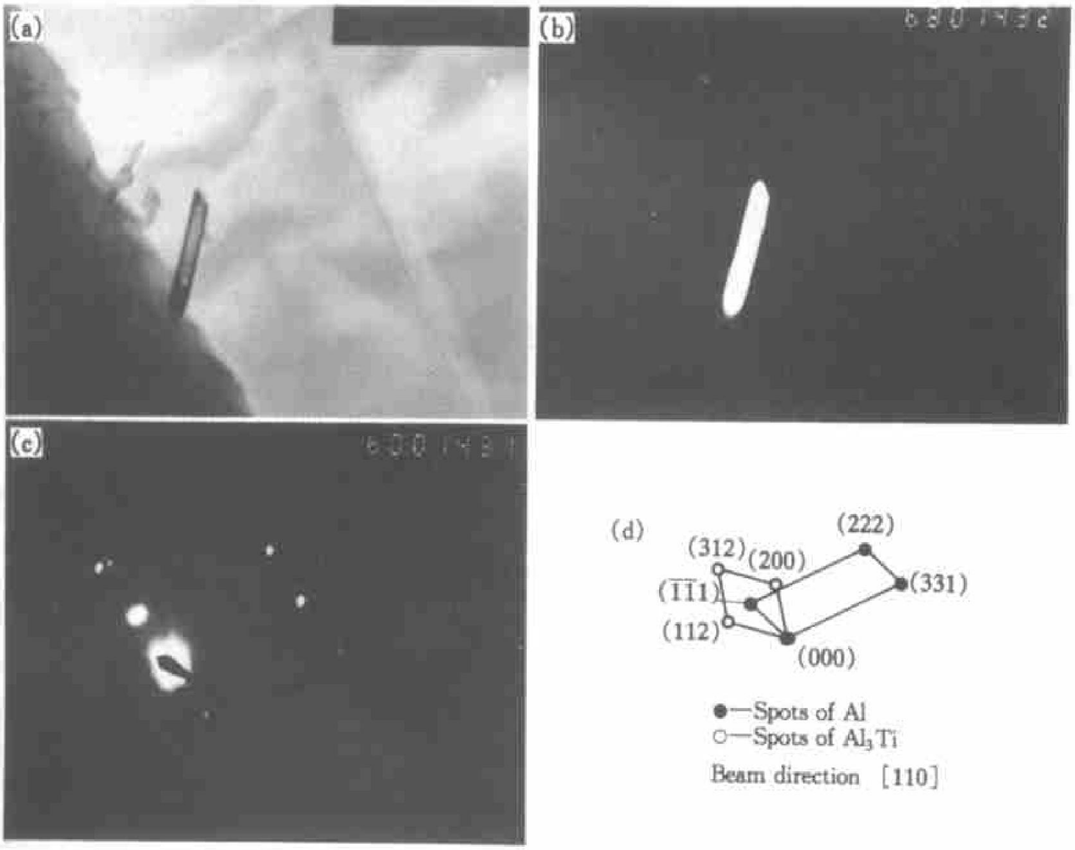

Fig. 7 TEM morphologies of Al_3Ti in Al_3Ti/ZL101 in-situ composite

(a) —Bright field; (b) —Dark field; (c) —Diffraction pattern; (d) —Indexing

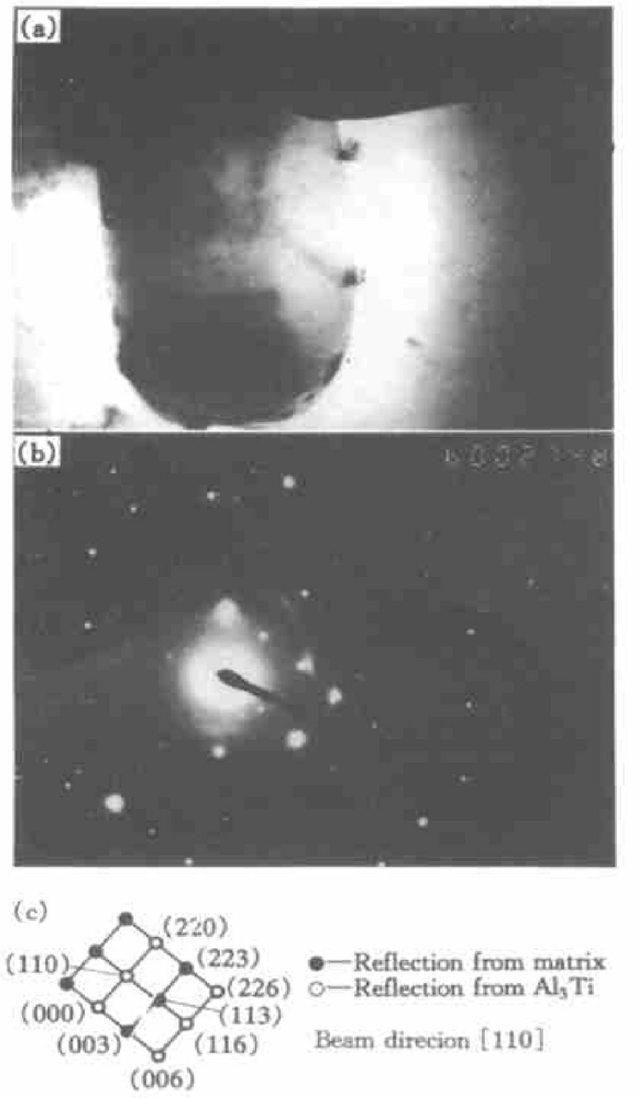

Fig. 8 TEM analysis images of Al_3Ti/ZL101 in-situ composite
(a) —Bright field; (b) —Diffraction pattern;
(c) —Indexing diffraction pattern

the grain size of Al_3Ti is less than 1 μm, fine grain strengthening caused by reinforcing phase plays a very important role[8, 9].

6.2 Dispersion strengthening

Reinforcing phase Al_3Ti is resulted from in-situ chemical reaction in aluminum alloy ZL101. It is uniformly distributed in α(Al) matrix, and plays the role of dispersion strengthening. Once Al_3Ti particles are formed from the reaction, it is neither dissolved to matrix nor reacted with the phase from matrix. In general case, the second kind of particles in the alloys strengthened by dispersion is those particle which can not be deformed[10].

6.3 Strengthening from dislocation multiplication

The elastic modulus of Al_3Ti is 166 GPa, while that of matrix is only 71 GPa, so that the deformation of matrix will be greater than that of Al_3Ti. But, coordinative deformation is necessary for both matrix and reinforcing phase. Thus, the side close to matrix in the interface will endure the pulling stress, while the side close to Al_3Ti will endure compressing stress, which will introduce a massive of dislocation around the reinforced phase, and result in a remarkable strengthening for the composite[11].

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