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The research of Ti-rich zone on the interface between TiC_x and aluminum melt and the formation of Ti_3Al in rapid solidified Al–Ti–C master alloys

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ABSTRACT

In the present work, the thermodynamic tendency of formation of Ti-rich zone on the interface between TiC_x and aluminum melt is calculated and a high titanium concentration can exist in the zone according to the thermodynamic calculation. Rapid solidified Al–5Ti–0.5C master alloy is analyzed by X-ray diffraction (XRD) and transmission electronic microscopy (TEM). The appearance of Ti_3Al in the master alloy results from the existence of high-concentration Ti-rich zone.

1. Introduction

Al–Ti–C master alloys have been used as a grain refiner in aluminum industry to achieve fine equiaxed grain structure and small grain size [1,2]. The grain size decreasing due to the addition of grain refiner can strengthen aluminum alloys and decrease shrinkage porosity, which will reduce the machining time and maintenance costs and prolong the tool life [3].

Several theories have been proposed to elucidate the mechanism for the refinement of Al by the addition of Al–Ti–C master alloys, such as peritectic theory, carbide particle theory and the peritectic "hulk" theory [4–6]. Despite these theories, recent researches have shown that the existence of excess titanium in Al–Ti–C master alloys plays an important role on the refinement efficiency of TiC particles [7]. Observation of the α-Al grain centers after the addition of Al–Ti–C master alloys shows that excess titanium segregates to the interface between TiC and aluminum melt, forming a Ti-rich zone around the particles [7,8]. From the above results, it can be assumed that there is a "Ti transition zone" formed on the interface between TiC and aluminum melt, which will evolve into the Ti transition layer in the state of solid after solidification [9].

Dariel et al. [10] researched the wetting of TiC by non-reactive liquid metals. The thermodynamic calculation indicates that segregation of titanium on the surface of TiC_x in the non-reactive metal melts (such as Cu, Ag, Au and Sn), resulting from the titanium equilibrium between TiC_x and non-reactive metal melts, helps the wetting of the TiC_x by non-reactive metals with a Ti-rich structure. This paper investigates the thermodynamic possibility of the formation of Ti-rich zone in Al–Ti–C system, by calculating the titanium equilibrium between carbide and aluminum melt.

Due to the difficulty of researching the liquid structure, rapid solidification technique was introduced to study the Ti-rich zone in Al–Ti–C master alloys, and the microstructure was analyzed to verify the thermodynamic calculation.

2. Thermodynamic considerations

2.1. Reaction between TiC and aluminum melt

The interaction between TiC and aluminum melt is complicated, and have been investigated a lot. In previous investigations, the interaction between TiC and molten aluminum was interpreted in terms of the thermodynamic properties in the Al-rich corner of the Al–Ti–C system. It is well demonstrated that liquid aluminum could coexist with Al_4C_3, TiC and $TiAl_3$, depending on the amount of titanium and carbon contained in the melt and the temperature [11]. For instance, at 1085 ± 15 K [12] or at 973 K [13], the invariant reaction:

$$TiC \Leftrightarrow TiAl_3 + Al_4C_3 \qquad (1)$$

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takes place in liquid aluminum and TiC is not stable below these temperatures. Banerji and Reif [14] calculated the transition temperature via the changes of Gibbs energy of TiC and Al_4C_3 in aluminum melt. The calculated transition temperature is about 1450 K, which means TiC is more stable than Al_4C_3 above this temperature and it is reversed below 1450 K.

Frage et al. [11] calculated the high-temperature phase equilibrium in the Al-rich corner of the Al–Ti–C system from 950 to 1400 K, showing that stoichiometric TiC is not stable in liquid aluminum. For example, a two-phase equilibrium between Al_L and TiC_x exists only in the $0.91 < x < 0.82$ range at 1300 K. Thus, the reaction of Al_L with stoichiometric TiC leads to the formation of the Al_4C_3 phase, whereas for $x < 0.82$, only the intermetallic compound $TiAl_3$ can be formed at this temperature.

Anyway, TiC is normally not stoichiometric. TiC_x is ($x = 0.48$–0.98) the usual form of TiC in Al–Ti–C system.

2.2. Equilibrium between titanium concentration in aluminum melt and TiC_x

Dariel et al. [10] have researched the titanium equilibrium between TiC_x and non-reaction metal melts, which indicated that a Ti-rich zone is necessary for the wetting of TiC_x. However, the titanium equilibrium between TiC_x and aluminum melt is not calculated and the appearance of the Ti-rich zone around TiC particles in refined α-Al grain centers is not explained theoretically, neither.

According to Dariel's calculation, the Ti-rich zone between TiC_x and aluminum melt may result from the carbon deficit in TiC_x, which leads to the change of chemical potential of titanium. In order to find the relationship between them, the titanium equilibrium should be calculated. Therefore, it is necessary to know the relationship between titanium activity and carbon content in TiC_x, the relationship between titanium activity and titanium concentration in aluminum melt and the relativity of titanium activities in TiC_x and aluminum melt.

The decrease of carbon content in the carbide phase leads to increased titanium activity and enhanced titanium transferring into the metallic (liquid) phase [11]. The titanium activity in sub-stoichiometric carbide as a function of a carbon-to-titanium ratio (C/Ti) = x, could be expressed as [15]:

$$\log a_{\mathrm{Ti}}^{\mathrm{S}} = \log(1-x) + \left(-\frac{13307.7}{T} + 2.96\right)x^2 + \frac{3063.7}{T} - 0.4 \quad (2)$$

For Eq. (2), the standard state is pure β-titanium.

In order to calculate the titanium concentration in aluminum melt, it is necessary to know the titanium activity and activity coefficient. The titanium activity coefficient can be expressed as [16]:

$$RT\ln\gamma_{\mathrm{Ti}} = RT\ln\gamma_{\mathrm{Ti}}|x_{\mathrm{Ti}=0} = -113,400 + 37.800T \quad (3)$$

And the titanium activity in aluminum melt could be calculated by means of the relativity of titanium activity in TiC_x and aluminum melt under equilibrium state.

The chemical potentials of titanium in TiC_x and aluminum melt are equal, thus:

$$\mu_{\mathrm{Ti}}^{\mathrm{S}} = \mu_{\mathrm{Ti}}^{\mathrm{L}} \quad (4)$$

and

$$\mu_{\mathrm{Ti}}^{\mathrm{S}} = (\mu_{\mathrm{Ti}}^{\mathrm{S}})^0 + RT\ln a_{\mathrm{Ti}}^{\mathrm{S}}, \qquad \mu_{\mathrm{Ti}}^{\mathrm{L}} = (\mu_{\mathrm{Ti}}^{\mathrm{L}})^0 + RT\ln a_{\mathrm{Ti}}^{\mathrm{L}} \quad (5)$$

From Eqs. (4) and (5), one obtains:

$$(\mu_{\mathrm{Ti}}^{\mathrm{S}})^0 - (\mu_{\mathrm{Ti}}^{\mathrm{L}})^0 = RT\ln\frac{a_{\mathrm{Ti}}^{\mathrm{L}}}{a_{\mathrm{Ti}}^{\mathrm{S}}} \quad (6)$$

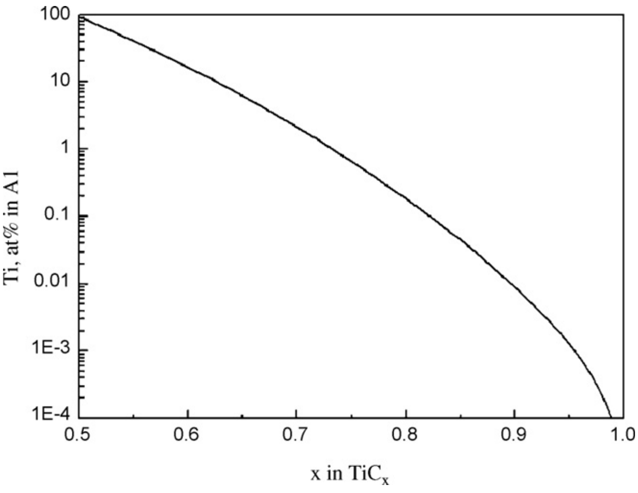

Fig. 1. The calculated equilibrium titanium content in aluminum melt as a function of the carbide composition.

where μ^0 is the chemical potentials in the standard state, and $a_{\mathrm{Ti}}^{\mathrm{S}}$, $a_{\mathrm{Ti}}^{\mathrm{L}}$ are the titanium activities in the carbide and aluminum melt, respectively.

Make

$$\Delta\mu_{\mathrm{Ti}}^0 = (\mu_{\mathrm{Ti}}^{\mathrm{S}})^0 - (\mu_{\mathrm{Ti}}^{\mathrm{L}})^0 \quad (7)$$

$\Delta\mu_{\mathrm{Ti}}^0$ is the change of chemical potential of titanium associated with different standard states. So:

$$\Delta\mu_{\mathrm{Ti}}^0 = \Delta G_{\mathrm{TI}}^{\beta\to\mathrm{L}} = \Delta H_{\mathrm{Ti}}^{\beta\to\mathrm{L}} - T\frac{\Delta H_{\mathrm{Ti}}^{\beta\to\mathrm{L}}}{T_{\mathrm{Ti,f}}} = 16218 - 8.36T(\mathrm{J/mol}) \quad (8)$$

where $\Delta G_{\mathrm{TI}}^{\beta\to\mathrm{L}}$ and $\Delta H_{\mathrm{Ti}}^{\beta\to\mathrm{L}}$ are the changes in the Gibbs free energy and enthalpy, respectively, and $T_{\mathrm{Ti,f}} = 1940$ K is its normal melting point.

Using Eqs. (2)–(8), the equilibrium titanium concentration in the aluminum melt as a function of TiC_x composition was calculated. Eq. (9) shows the equation, X_{Ti} is the atom concentration:

$$X_{\mathrm{Ti}} = \frac{a_{\mathrm{Ti}}^{\mathrm{L}}}{\gamma_{\mathrm{Ti}}} = 10\hat{}\left[\log(1-x) + \left(-\frac{13307.7}{T} + 2.96\right)x^2 + \frac{3063.7}{T} - 0.4\right] \times \frac{\exp((1950.68/T) - 1.01)}{\exp((-13639.64/T) + 4.55)} \quad (9)$$

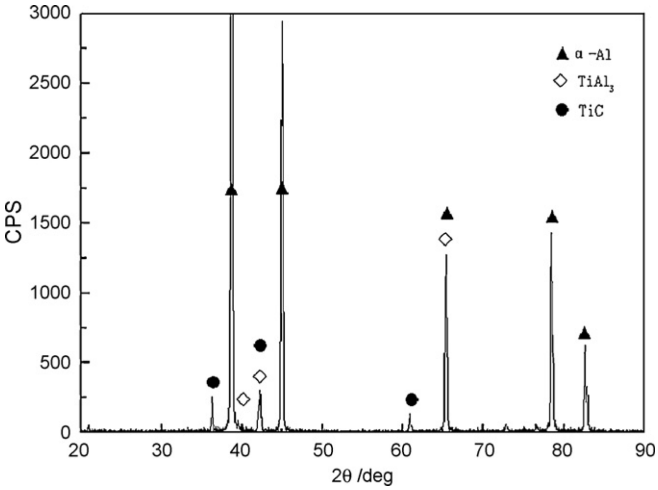

Fig. 2. XRD patterns of rapid solidified master alloy.

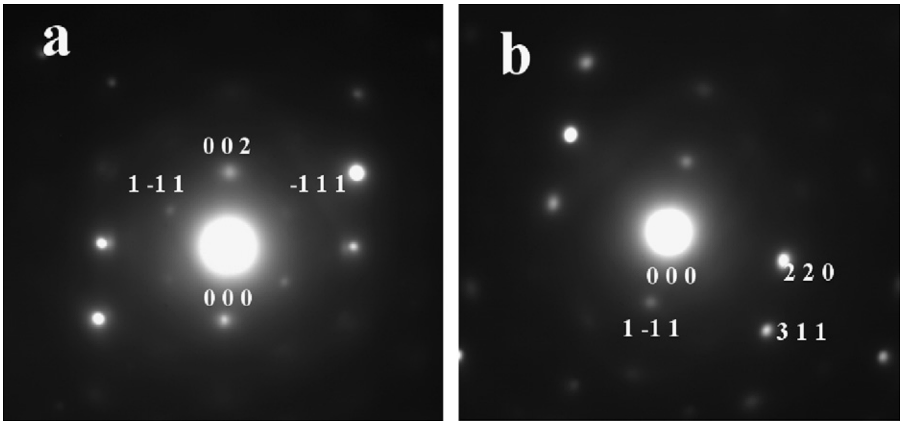

Fig. 3. (a) TiC [1 1 0] and Al [2 1 0] ZA SAED patterns; (b) $TiAl_3$ [−1 1 2] ZA SAED pattern.

The decrease in the carbon content in the carbide phase leads to a significant increase in the titanium content in the liquid metals. The calculated titanium concentration at 1500 K is shown in Fig. 1.

3. Experimental verification

Al–5Ti–0.5C master alloy was manufactured in a high frequency furnace with graphite powders (average particle size: 10 μm), Al–10Ti master alloys and high purity aluminum (99.9%). Al–10Ti master alloys and high purity aluminum were heated up to 1973 K in the high frequency furnace. After the melting process, graphite powders were directly added into the melt and kept for 3 min. Then the mixed melt was poured into a graphite mold.

The master alloy was heated up to 1673 K and cast into continuous ribbons using the single roller melt spinning technique under a partial argon atmosphere. A wheel speed of 1000 revolutions per minute (rpm), corresponding to a tangential speed of ∼18 m/s, was adopted to make the ribbons 30–50 μm in thickness and 3–5 mm in width. The phases and microstructure were characterized by X-ray diffraction (XRD) and transmission electronic microscopy (TEM) analysis. All the temperatures were measured by an infra-red thermometer, and the accuracy was about ±100 K.

Fig. 2 shows the XRD patterns of the rapid solidified master alloy with α-Al, $TiAl_3$ and TiC in it. It is obvious that most of the excess titanium exists as $TiAl_3$.

The microstructure of the rapid solidified Al–5Ti–0.5C master alloys are analyzed by TEM. Fig. 3(a) and (b) shows the selected-area

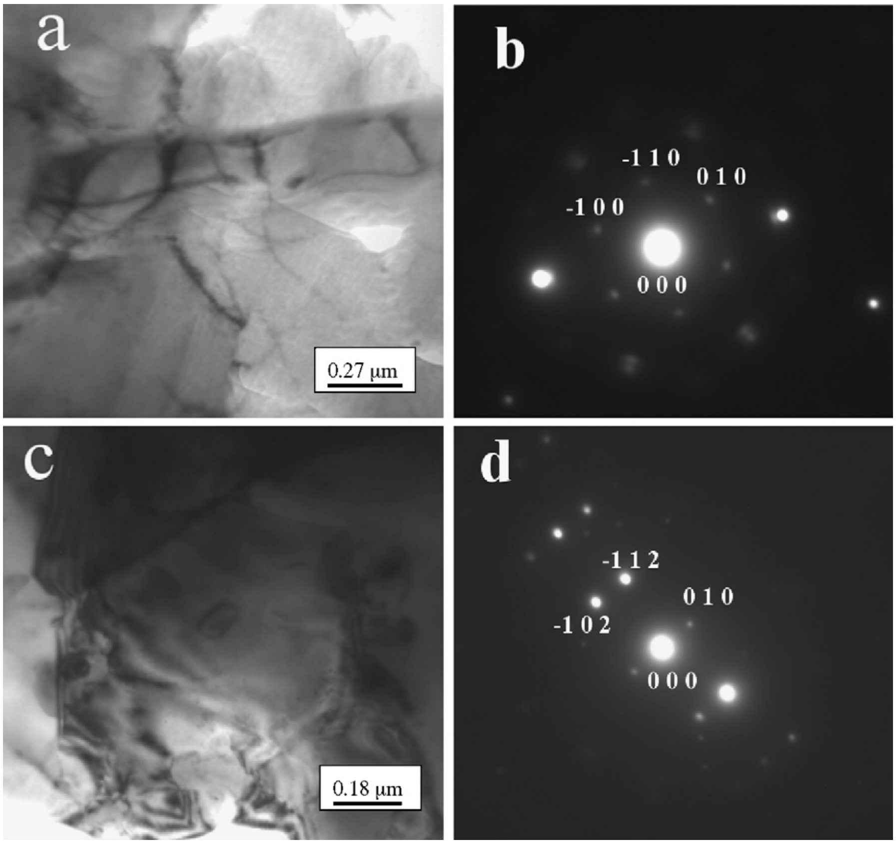

Fig. 4. (a) TEM bright-field image of Ti_3Al; (b) Ti_3Al [0 0 1] and Al [1 1 1] ZA SAED patterns; (c) TEM bright-field image of Ti_3Al; (d) Ti_3Al [2 0 1] ZA SAED pattern.

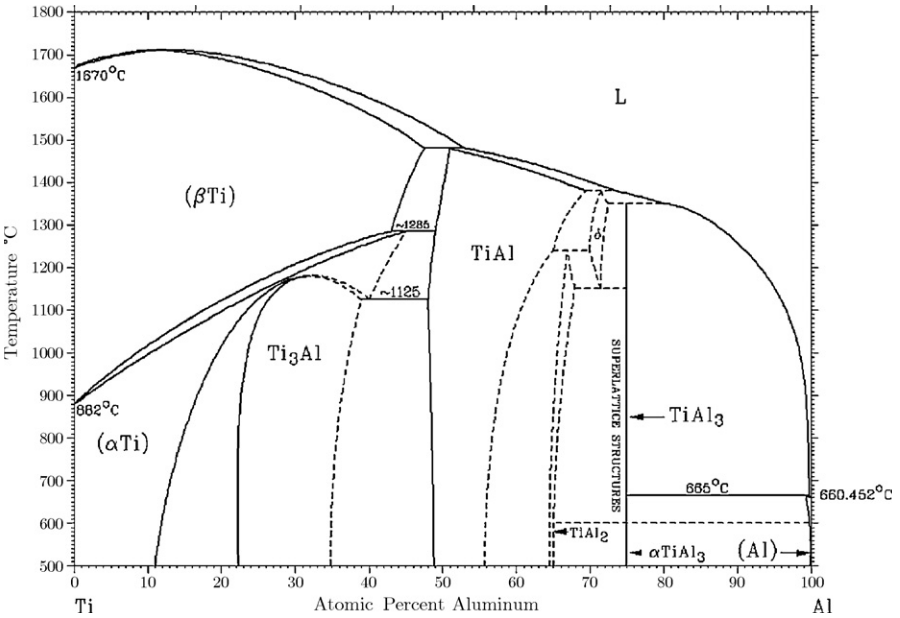

Fig. 5. Phase diagram of Al–Ti system.

electron diffraction (SAED) patterns of TiC in zone axis of [1 1 0] and $TiAl_3$ in zone axis of [−1 1 2], respectively. And Al [2 1 0] ZA SAED pattern was also showed in Fig. 3(a).

Not only TiC, but also Ti_3Al was found by TEM analysis. Fig. 4(a) and (c) is the bright-field image of Ti_3Al, and Fig. 4(b) is the corresponding Ti_3Al [0 0 1] ZA SAED pattern of (a). Fig. 4(d) is the corresponding Ti_3Al [2 0 1] ZA SAED pattern of (c). Also Al [1 1 1] ZA SAED pattern was showed in Fig. 4(b). Ti_3Al was not detected by XRD analysis, but was found by TEM. The SAED patterns indicated the existence of Ti_3Al. As most of the excess titanium exists as $TiAl_3$, there is only a little amount of Ti_3Al in the Al–Ti–C master alloy. Ti_3Al could not be detected by XRD if the amount is lower than that is required. Therefore, it does not appear in the XRD analysis.

Fig. 5 shows the phase diagram of Al–Ti system. It is obvious that the formation of Ti_3Al requires high titanium concentration even up to 65–78 atomic percentages. The presence of Ti_3Al proves the existence of Ti-rich zone in Al–5Ti–0.5C melt, and the concentration is high enough to precipitate Ti_3Al. There is not enough time for titanium in high-concentration zone to diffuse into aluminum melt around when the master alloy is rapid solidified, so that excess titanium precipitates as Ti_3Al.

Many researches have been made on the rapid solidified Al–Ti–C master alloys, such as Ref. [17], but few of them have reported the formation of Ti_3Al. It is much easier for excess titanium to precipitate as $TiAl_3$ rather than Ti_3Al, under ordinary solidification conditions, because the formation of Ti_3Al requires high titanium concentration, as indicated in Fig. 5. There must be a reason for the formation of high titanium concentration zone in Al–5Ti–0.5C master alloys, which leads to the formation of Ti_3Al in rapid solidified alloys.

Fig. 1 shows the result of calculated equilibrium titanium concentration on the interface of TiC and aluminum melt, as a function of TiC composition. It demonstrates that the titanium concentration around TiC_x particles in aluminum melt increases while the carbon content in TiC_x decreases. Hence, the Ti-rich zones are formed on the interface of TiC_x and aluminum melt under equilibrium state, which has been proved by the formation of Ti-rich structure around TiC particles in α-Al grain centers after the addition of Al–Ti–C master alloy, reported in Refs. [7–9]. When the x in TiC_x is very low, 0.5 for instance, it is possible that titanium concentration can reach the level required by the precipitation of Ti_3Al, as indicated in Fig. 1, leading to the formation of Ti_3Al during rapid solidification process.

It is very difficult to identify the x in TiC_x in Al–Ti–C master alloys directly. Dubois et al. [18] have reported that TiC grains nucleate with very poor carbon content, and the carbon content in TiC increases with the progress of reaction. This result is in good agreement with the Ti–C phase diagram [19] where TiC germs, formed from the liquid at a temperature lower than 2773 K, present a large carbon deficit. Dariel et al.'s [11] calculation also indicates that TiC is off stoichiometric in Al–5Ti–0.5C system. They [10] have verified the relativity between lattice parameter and carbon content of titanium carbide phase. However, the lattice parameter measurements show only the average carbon content of the TiC_x particles in the master alloy, but the carbon content is not uniform in all the TiC_x particles. It is difficult to identify the TiC_x particles with significant carbon deficit, which lead to the formation of Ti_3Al, by the lattice parameter measurements.

The presented Al–5Ti–0.5C master alloy is manufactured within 3 min, and it is possible that parts of the particles present a large carbon deficit, which leads to the segregation of excess titanium around TiC_x, forming Ti_3Al during rapid solidification process.

4. Conclusion

Thermodynamic analysis of the equilibrium titanium content on the interface of TiC and aluminum melt, as a function of carbon content in substoichiometric TiC, provides a theoretical foundation for the explanation of Ti-rich zone in Al–Ti–C system. TiC is normally substoichiometric in Al–Ti–C master alloys, which results to the segregation of excess titanium around TiC particles to reach the equilibrium state, forming Ti-rich zone. Even high titanium concentration can be achieved when the x in TiC_x is very low, as calculated. The Ti-rich structure in α-Al grain centers after the refinement by Al–Ti–C master alloy proved the thermodynamic calculation result.

The presence of substoichiometric TiC, such as TiC_x (x = 0.48–0.98), results in the formation of Ti-rich zone on the interface of TiC_x and aluminum melt, because of the driving force supplied by titanium equilibrium between TiC_x and aluminum melt. Titanium in high titanium concentration zone is not able to diffuse around in aluminum melt during rapid solidification process, precipitating Ti_3Al instead. The appearance of Ti_3Al

in the rapid solidified master alloy reflects the existence of high-concentration Ti-rich zone, verifying the thermodynamic calculation.

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