Materials

Effect of Ti/B Additions on the Formation of Al₃Ti of *in situ* TiB₂/Al Composites

Bin Yang, Jishan Zhang, Xianjin Duan, Shuangchun Hu

State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, China
(Received 1999-03-31)

Abstract: A novel technique for fabricating TiB_2/Al composites in molten aluminum was introduced. The formation mechanism of brittle Al_3Ti particulates up to 30 μm in size produced in the composites was studied and a method of eliminating them was proposed. The results show that (1) the brittle Al_3Ti particulates are always present in the composites when the molar ratio of Ti to B $n_{Ti}:n_B$ is 1:2; and (2) the formation of the brittle Al_3Ti phase can be avoided entirely from the final product by using a proper $n_{Ti}:n_B$ of 1:4 in the Ti-B-Al preforms. In the former case, the tensile elongation of the composite is only 4%, much lower than the value of pure aluminum (20%). In the later case, the tensile elongation of this composite is 10%, higher than the value of the composite with a lot of Al_3Ti (4%), whereas the ultimate tensile strength of the former is nearly that of the later.

Key words: *In situ* reaction; TiB_2/Al composites; Al_3Ti phase

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Particulate reinforced Metal Matrix Composites (MMCs) show great potential for structural materials due to their promising specific strength and modulus. Among the numerous technologies producing particulate reinforced MMCs, those allowing *in situ* production of the reinforcement offer significant advantages from technical and economic standpoint. Some of these technologies include Self-propagating High-temperature Synthesis (SHS), Exothermic Dispersion (ED), reactions and reactive gas infiltration [1–12]. However, the most effective way to obtain low cost MMCs is *via* casting process. Recently, reference [13] used a novel technique — melt *in situ* reaction processing (MIRP) — to generate fine particulates in aluminum matrix. Apart from the intrinsic advantages of *in situ* synthesis, this new technique has also a number of advantages: (1) the reinforcing particulates are formed *in situ* in a molten alloy and the melt containing the dispersion is cast into an ingot for subsequent fabrication into wrought products; (2) the reaction is typically accomplished at a lower temperature (760–900℃) and within a very short time, showing that the process is cost effective and easy to control; and (3) the identification of conditions whereby good dispersions of the reinforcement in the molten alloy can be maintained, and porosity and detrimental matrix-reinforcement reactions can be minimized, which are essential to the development of production routes based on this approach. The technique, based on this investigation, is promising for mass production of aluminum matrix composite by virtue of its low production cost, high production rate and a strong possibility of near-net shape forming.

Titanium diboride, which has great potential not only as a refractory material, but also as an electronic material because of its high melting point, hardness, electrical conductivity and thermal conductivity, has been widely used to metal matrix composites as the reinforcement phase [14]. However, unwanted brittle Al_3Ti particulates, up to 30 μm in size, are always present in the composite when the molar ratio of Ti to B $n_{Ti}:n_B$ is 1:2 leading to poor plasticity of the composites. At present, there is very little information available on how to eliminate the brittle Al_3Ti phase [14]. The purpose of this study is to find, based upon the thermodynamic data, a method of precluding the Al_3Ti in order to improve the plasticity of the aluminum matrix composites.

1 Experimental Method

The reagents used in this research consisted of elemental powders of Ti (96%, < 75 μm), B (95%, < 10 μm) and Al (99%, < 75 μm). The powders with different $n_{Ti}:n_B$ plus Al (5%–80% in mass fraction) were mixed by dry milling with steel balls for 10 h in a stainless steel container. Then, the powder mixture was mechanically pressed into a cylindrical preform using a pressure near 40 MPa. The green preforms were 20 mm in diameter and 25 mm in height. About 900 g of commercial aluminum was melted in a graphite crucible. Then, 3% preforms (in mass fraction) were inserted into the molten aluminum held at 900℃. When all reactions were completed (the end point of the reaction can be determined by observing the evidence of a dazzling light originated from the reacted melt pool [13]), the

melt was stirred at the time when temperature of the melted solution decreased to 730℃. It is worth noting that the processes mentioned previously were carried out in air. The TiB$_2$/Al composite was obtained finally by pouring the melt into a steel mould at room temperature.

The composite products were analysed by X-ray Diffraction (XRD) for the phase determination. Their microstructures were examined with Optical Microscopy (OM), and Scanning Electron Microscopy (SEM) with an Energy Dispersive Spectroscopy (EDS) facility. The speciments were etched in a solution of mixed acids (2HF+3HCl+5HNO$_4$+250H$_2$O in ml). The tensile properties of the TiB$_2$/Al composites with or without Al$_3$Ti were also studied using an Instron test machine at a constant crosshead speed of 0.5 mm/min. Tensile testing specimens with a 3 mm gauge width and a 3 mm gauge length were tested at room temperature.

2 Results

The XRD pattern (**figure 1**) reveals that there are four phases, *i.e.*, TiB$_2$, Al, Al$_3$Ti and Al$_2$O$_3$, in the composite. TiB$_2$, Al$_3$Ti and Al$_2$O$_3$ were not added to the powder mixture and they appear to have been formed during the process. The mechanisms of formation of the TiB$_2$ and Al$_2$O$_3$ have been discussed in detail in reference [13]. **Figure 2** shows a typical SEM photomicrograph of the Al$_3$Ti. It indicates that the Al$_3$Ti is generally in strip or rectangular shape. The size of most Al$_3$Ti is over 30 μm. The composition of the Al$_3$Ti phase determined by EDS is shown in **figure 3**.
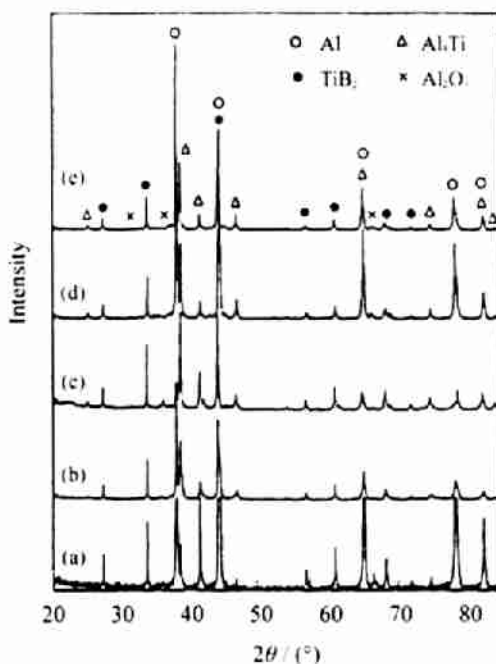

Figure 2 SEM micrograph of the Al$_3$Ti in the TiB$_2$/Al composite produced *via* n_{Ti}:n_B = 1:2.
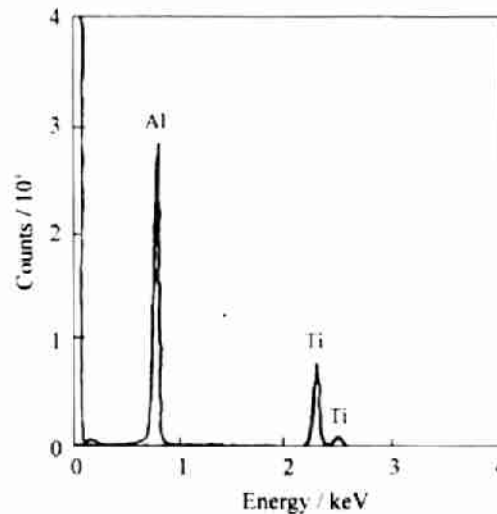
Element	Spectrum type	Mass fraction /%	Molar fraction /%
Al	ED	62.54	74.77
Ti	ED	37.46	25.24

Figure 3 Composition of the Al$_3$Ti phase determined by EDS.

The tensile experimental results (**table 1**) show that the TiB$_2$/Al composites exhibit much higher strength than the value of pure aluminum. However, the tensile elongation of 3%TiB$_2$/Al composite (in mass fraction, always allowed) with a lot of Al$_3$Ti particulates was only 4%, much lower than the value of pure aluminum (20%). Moreover, the higher the titanium content, the greater the tendency for rectangular Al$_3$Ti phase to form in aluminum matrix. It indicates that the titanium content in the preforms with n_{Ti}:n_B=1:2 is relatively excessive. Therefore, other experiments were performed in which n_{Ti}:n_B in the preforms was 1:4. **Figure 4** showed the phase compositions of the composite. One can see that the Al$_3$Ti is absent in the final product within the precision of the X-ray method. Optical micrograph of the composite produced in this case is shown in **figure 5** where no Al$_3$Ti phase can be found. The tensile elongation of this composite was 10% (table 1), higher than the value of the composite with a lot of Al$_3$Ti (4%), whereas the ultimate tensile strength of the former is

Figure 1 XRD patterns of the composite with n_{Ti}:n_B = 1:2 and (a) 5.0%Al, (b) 30%Al, (c) 40%Al, (d) 70%Al and (e) 80%Al in the preforms (mass fraction).
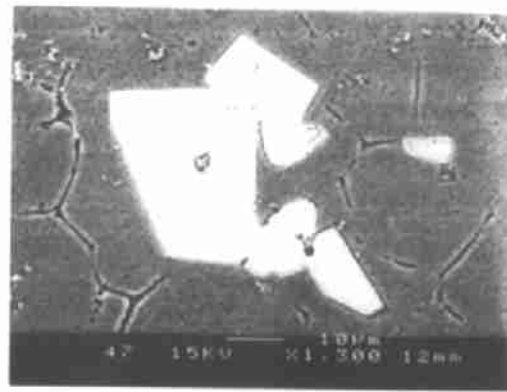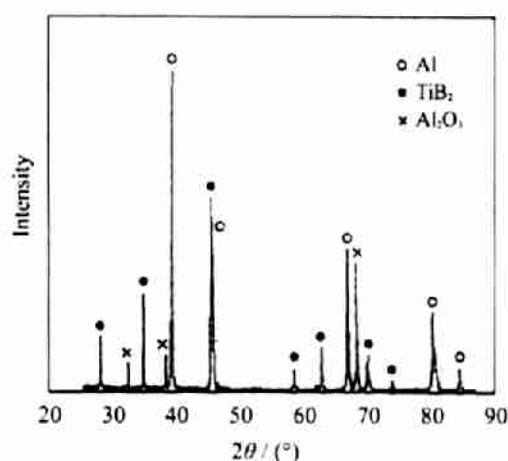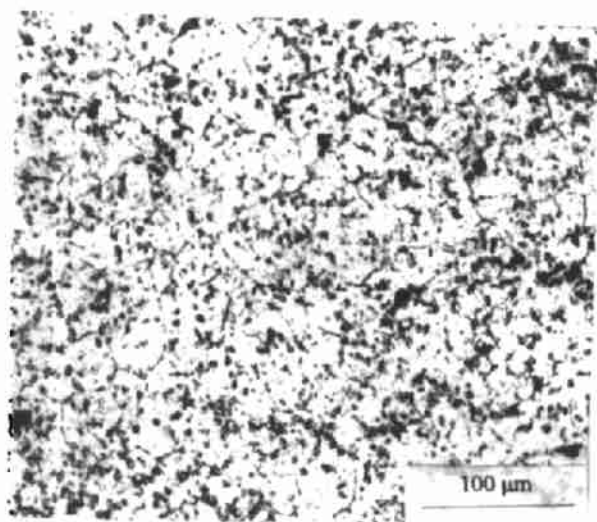
nearly that of the latter.

Table 1 Tensile properties of the TiB$_2$/Al composite.

Material	Ultimate tensile strength / MPa	Tensile elongation / %
Al-3%TiB$_2$ composite with Al$_3$Ti	151.0	4
Al-3%TiB$_2$ composite without Al$_3$Ti	147.3	10
Commercial Al*	97.3	20

Note: * represents the values from reference [15].

Figure 4 XRD pattern of the composite with $n_{Ti}:n_B=1:4$ and $w_A=40\%$ in the preform.

Figure 5 Optical micrograph of the TiB$_2$/Al composite produced via $n_{Ti}:n_B=1:4$.

3 Discussion

It is clear that Al$_3$Ti particulates in the composite come from Ti-B-Al preforms. Strictly speaking, the formation of Al$_3$Ti in Ti-B-Al preforms is a non-equilibrium process. However, it is difficult to determine thermal quantity removing from the preforms. In these calculations, it is assumed that the heat generated by the formation of Al$_3$Ti goes only to raise the tempera-

ture of the product and there is no loss of heat to the surroundings, meaning it is a "closed system". In addition, it is also assumed that the reaction goes to completion. Thus, the adiabatic temperature T_{ad} can be calculated from the heat balance condition [3]:

$$-\Delta H_{T_r}^\ominus = \int_{T_r}^{T_{ad}} c_p \, dT \tag{1}$$

where $\Delta H_{T_r}^\ominus$ is the enthalpy of formation of Al$_3$Ti at T_0, and c_p the heat capacity of the solid Al$_3$Ti. T_0 is typically taken as 298 K, and the heat generated by the reaction is the standard heat of formation of the product. In practice, however, the reaction is not initiated at room temperature but at some elevated temperature. This will influence the results. When the elevated temperature is chosen at 900℃, i.e., the temperature of the molten aluminum into which the preforms are introduced, the fraction of the molten Al$_3$Ti, γ, will certainly be larger than that of the molten Al$_3$Ti produced at 660 ℃, i.e., the melting point of aluminum. In order to make the calculated results to be representative, the melting point of aluminum is chosen at initiate reaction temperature.

The following equations can be obtained by preliminary calculations:

$$-\Delta H_{f,T_{m,Al}}^\ominus > \int_{T_{m,Al}}^{T_m} c_p \, dT \tag{2}$$

$$-\Delta H_{f,T_{m,Al}}^\ominus < \int_{T_{m,Al}}^{T_m} c_p \, dT + \Delta H_m \tag{3}$$

where, ΔH_m and $\Delta H_{f,T_{m,Al}}^\ominus$ are the enthalpy of fusion of Al$_3$Ti, the enthalpy of formation of Al$_3$Ti at the melting point of aluminum, respectively. T_m is the melting point of Al$_3$Ti, and $T_{m,Al}$ is the melting point of Al.

The calculated results show that the heat generated by producing the Al$_3$Ti makes partial Al$_3$Ti to be in the molten condition, therefore, Al$_3$Ti melting point itself is, in this case, the T_{ad}, and that the reaction temperature, in this case, is lower than the melting point of titanium (1680℃), thus the reaction $3Al_{(l)}+Ti_{(s)} \rightarrow Al_3Ti$ can be written. Based upon the available thermodynamic theory, the following equations can be obtained:

$$-\Delta H_{f,T_{m,Al}}^\ominus = \int_{T_{m,Al}}^{T_m} c_{p,S} \, dT + \gamma \Delta H_m \tag{4}$$

$$-\Delta H_{f,T_{m,Al}}^\ominus = -\Delta H_{f,298}^\ominus + \int_{298}^{T_{m,Al}} (c_{p,S} - c_{p,Al} - c_{p,Ti}) \, dT \tag{5}$$

where, $\Delta H_{f,298}^\ominus$ is the enthalpy of reaction at 298K, γ is the fraction of molten Al$_3$Ti, $c_{p,S}$ is the heat capacity of solid Al$_3$Ti, $c_{p,Al}$ is the heat capacity of liquid Al, and $c_{p,Ti}$ is the heat capacity of solid Ti. $c_{p,S} - c_{p,Al} - c_{p,Ti} = -12.774 + 55.631 \times 10^{-3} T - 1.825 \times 10^5 T^{-2} - 62.259 \times 10^{-6} T^2$ (J·K^{-1}mol^{-1}) [16].

The thermodynamic data of the Al$_3$Ti for the calculations are listed in **table 2** [16,17]. From equations (1) and (2), γ equals approximately 85%. The calculated

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Table 2 Thermodynamic data of Al₃Ti.

T_m / K	1 613
ΔH_m / kJ·mol^{-1}	80
$\Delta H^0_{f(298)}$ / kJ·mol^{-1}	−142.25
$c_{p,S}$ / J·(K·mol)$^{-1}$	$103.512 + 16.736 \times 10^{-3}\,T - 8.996 \times 10^{5}\,T^{-2}$

results indicate that the heat generated by the formation of Al₃Ti makes Al₃Ti to be partially melted. At this time, the boron atoms can diffuse into the molten Al₃Ti to form some TiB₂ particulates by the reaction Al₃Ti+ 2B→3Al+TiB₂ [13]. The reason why Al₃Ti is precluded entirely in the final product when n_{Ti}:n_B is 1:4 is that the reaction Ti+2B→TiB₂ performed during final stage can, in this case, take place more completely than in the case of n_{Ti}:n_B=1:2. The heat generated in the system is so high that it can melt all of Al₃Ti produced during initial stage. Therefore, boron atoms can diffuse further into the molten Al₃Ti to form TiB₂-Al solution. On the other hand, the Al₃Ti can decompose owing to a large amount of heat released in the formation of TiB₂, thus the brittle Al₃Ti is entirely absent in the final products. In this case, the tensile elongation of the composite is 10%, higher than the value of the composite with a lot of Al₃Ti (4%), whereas the ultimate tensile strength of the former is nearly that of the latter.

4 Conclusions

(1) Al₃Ti is always present in the final product when n_{Ti}:n_B=1: 2. In this case, the tensile elongation of the composite is only 4%, much lower than the value of pure aluminum (20%).

(2) The brittle Al₃Ti phase can be entirely eliminated from the final alloy by using a n_{Ti}:n_B=1:4 in the starting mixture. The tensile elongation of this composite is 10%, higher than the value of the composite with a lot of Al₃Ti (4%), whereas the ultimate tensile strength of the former is nearly that of the latter.

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