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Formation of composites fabricated by exothermic dispersion reaction in Al-TiO_2-B_2O_3 system

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Abstract: The formation of aluminum matrix composites fabricated by exothermic dispersion reaction in Al-TiO_2-B_2O_3 system was investigated. The thermal analysis results show that the reactions are spontaneous and exothermic. The Gibbs free energy of α-Al_2O_3 is the lowest among all the combustion products, followed by TiB_2 and Al_3Ti. It is noted that when the B_2O_3/TiO_2 mole ratio is below 1, the reaction products are composed of particle-like α-Al_2O_3, TiB_2 and rod-like Al_3Ti. The α-Al_2O_3 crystallites, resulting from the reaction between Al and TiO_2 or B_2O_3, are segregated at the grain boundaries due to a lower wettability with the matrix. SEM micrographs show that rod-like Al_3Ti phase distributes uniformly in the matrix. When the B_2O_3/TiO_2 mole ratio is around 1, the Al_3Ti phase almost disappears in the composites, and the distribution of α-Al_2O_3 particulates is improved evidently.

Key words: aluminum matrix composite; reaction mechanism; mole ratio; exothermic dispersion reaction

1 Introduction

In situ synthesis techniques are derived from the self-propagating combustion, which is used for fabricating metal or ceramic matrix composites. As the reinforcements are generated directly from chemical reaction within the matrix, the composites are of many excellent advantages, such as clean reinforcement-matrix interface, fine and thermodynamically stable reinforcements, good compatibility and high bond strength between reinforcements and the matrix, and low fabrication costs. It is eventual and critical to select a suitable reaction system and corresponded reaction method. There are several methods reported previously, such as self-propagating high temperature synthesis (SHS), direct metal oxidation method (DIMOX), exothermic dispersion(XD), mechanical alloying(MA), and pressureless metal infiltration(PRRIMX)[1−3]. Recently, the XD method has been focused extensively for it can produce fine ceramic particles (＜1 μm) and the volume frication of the reinforcement can vary in a wide range. Among these reinforcements, titanium diboride (TiB_2) is compatible with aluminum matrix, and does not react with aluminum. In this case, it provides a method to avoid the formation of brittle products at the particles/matrix interface, which improves the interface bonding strength. Furthermore, TiB_2 exhibits very high stiffness and hardness. Considering such excellent characteristics, TiB_2 phase has been used increasingly as reinforcements in aluminum-based metal matrix composites(MMCs)[4−5].

Researchers have chosen the reaction systems like Al-Ti, Al-B, Al-Ti-C, Al-Ti-B and Al-Zr-O[6−10], for the fabrication of Al-based MMCs. To decrease the processing cost, the Ti and B were substituted with the compounds of TiO_2 and B_2O_3 respectively. Therefore, the Al-TiO_2-B_2O_3, Al-TiO_2-B and Al-TiO_2-C reaction systems were highlighted recently. This work aims to investigate the formation of Al_2O_3, Al_3Ti and TiB_2 in the Al-based MMCs fabricated by XD method in Al-TiO_2-B_2O_3 system.

2 Experimental

The titanium dioxide TiO_2 powder (98% purity,

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manufactured by Guangdong Guanghua Chemistry Factory Co., Ltd., Guangdong, China), and pure aluminum Al powder (99.6% puring, supplied by Shanghai Refined Chemistry Industry Science & Technology Co., Ltd. Shanghai, China), and Boric oxide B_2O_3 powder (98.0% purity, made by Shanghai Tongya Refined Chemistry Industry Factory, Shanghai, China) with an average size of 3−5 μm, 30−50 μm and 20−30 μm, respectively, were used as raw materials. According to stoichiometric calculation, the mixed powders with 30% (volume fraction) reinforcements whose B_2O_3/TiO_2 mole ratios were 0, 0.5 and 1.0 respectively were mixed by a ball-milling in the stainless steel vacuum jar for 2 h, and then cold compacted into green billets with a diameter of 30 mm. When the compacts were heated in vacuum furnace one by one at about 1 073 K, the combustion reaction occurred and held for about 10 min, and then the combusted compacts were cooled down to room temperature in the furnace. The three samples A ($r(B_2O_3/TiO_2)$=0), B ($r(B_2O_3/TiO_2)$=0.5) and C ($r(B_2O_3/TiO_2)$=1) made from the reacted compacts were mechanically polished and then investigated by X-ray diffraction(XRD), scanning electron microscope(SEM) and energy dispersive spectrum(EDS).

3 Result and discussion

3.1 Thermodynamic analysis

When the temperature of furnace is increased to about 1 073 K, the B_2O_3 and Al powders in the compact are melted firstly, and then Al-TiO_2 liquid-solid and Al-B_2O_3 liquid-liquid interfaces are formed. The reactions occur as follows:

$$4Al+3TiO_2 \rightarrow 2\alpha\text{-}Al_2O_3+3[Ti] \quad (1)$$

$$\Delta G_T^0 = -53\,503+27.20T$$

$$\Delta H_T^0 = -943\,342-13.89T$$

$$2Al+B_2O_3 \rightarrow \alpha\text{-}Al_2O_3+2[B] \quad (2)$$

$$\Delta G_T^0 = -446\,226+131.64T$$

$$\Delta H_T^0 = -332\,685-146T$$

The above reactions are exothermic and their theoretical combustion temperature can be calculated by the following formula:

$$\sum n_i (H_{T_{ad}}^0 - H_{298}^0)_{iP} = \sum n_i (H_T^0 - H_{298}^0)_{iR} - \Delta H_{298}^0 \quad (3)$$

where T is the preheating temperature; T_{ad} is the theoretic combustion temperature, n is the amount of substance, p is the products and R is the reactants.

The T_{ad} of the reactions (1) and (2) is 2 036 K and 2 213 K if not considering the aluminum matrix absorbing thermal. In fact, the T_{ad} of the reactions are 1 856 K and 2 045 K respectively which are lower than the previous figures. Therefore, the T_{ad} of the reactions (1) and (2) are all higher than the critical temperature 1 800 K that makes the combustion self- maintained. Due to the above reactions, an Al-Ti-B-α-Al_2O_3 reaction system is formed. Because the α-Al_2O_3 phase is very steady due to its low Gibbs free energy, the Al-Ti-B-α-Al_2O_3 quaternary system is equal to Al-Ti-B ternary system and the following reactions (3)−(8) are likely to occur in the compact:

$$[Ti]+2[B] \rightarrow TiB_2$$

$$\Delta G_{TiB_2}^0 = -284\,500+20.5T \quad (4)$$

$$[Ti]+[B] \rightarrow TiB$$

$$\Delta G_{TiB}^0 = -53\,503+27.5T \quad (5)$$

$$2[B]+Al \rightarrow AlB_2$$

$$\Delta G_{AlB_2}^0 = -65\,557-5.5T \quad (6)$$

$$12[B]+Al \rightarrow AlB_{12}$$

$$\Delta G_{AlB_{12}}^0 = -220\,000+7.5T \quad (7)$$

$$Al+[Ti] \rightarrow Al_3Ti$$

$$\Delta G_{Al_3Ti}^0 = -144\,242+21T \quad (8)$$

$$Al+[Ti] \rightarrow AlTi$$

$$\Delta G_{AlTi}^0 = -59\,042+11.1T \quad (9)$$

Fig.1 shows the curves of the Gibbs free energy vs temperature of the above reactions. It is indicated that all the reactions can take place spontaneously due to their negative ΔG_T^0. It is also indicated that the stability of these products is in the following order: α-Al_2O_3 > TiB_2 > AlB_{12} > Al_3Ti > TiB > AlB_2 > TiAl. As shown in the Al-Ti phase diagram (see Fig.2), it can be inferred that Al and Ti can form many different kinds of products. But when the content of Ti is less than 36.5% (mass fraction) in the aluminum matrix, Ti will react with Al to

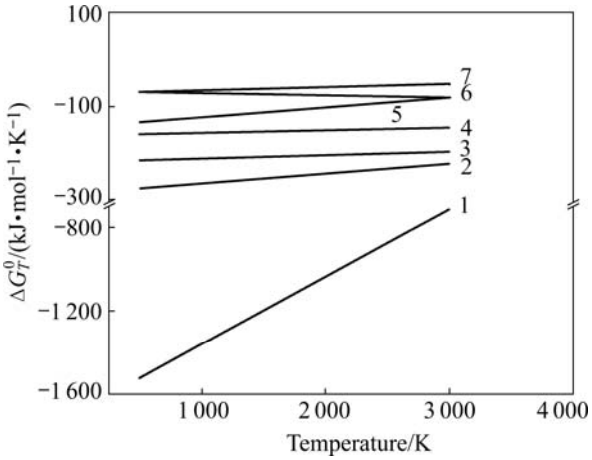


Fig.1 Gibbs free energies of possible combustion products vs temperature in Al-TiO_2- B_2O_3 system: 1 Al_2O_3; 2 TiB_2; 3 AlB_{12}; 4 TiB; 5 Ti_3Ti; 6 AlTi; 7 AlB_2

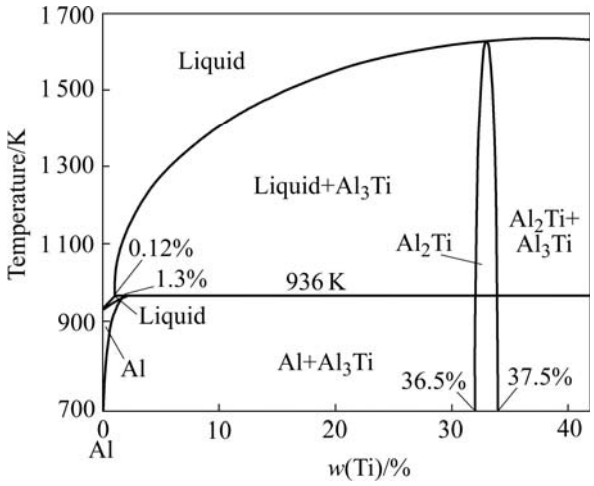


Fig.2 Al-Ti binary phase diagram

form Al_3Ti. In this experiment, the content of Ti is much less than 36.5% (mass fraction), therefore, Al_3Ti is formed.

In the Al-TiO_2-B_2O_3 system, the reaction equations vary with the B_2O_3/TiO_2 mole ratios as follows:

When $r(B_2O_3/TiO_2)=0$,

$$13Al+3TiO_2 \rightarrow 2\alpha\text{-}Al_2O_3+3Al_3Ti;$$

When $r(B_2O_3/TiO_2)=0.5$,

$$23Al+6TiO_2+3B_2O_3 \rightarrow 7\alpha\text{-}Al_2O_3+3Al_3Ti+3TiB_2;$$

When $r(B_2O_3/TiO_2)=1$,

$$10Al+3TiO_2+3B_2O_3 \rightarrow 5\alpha\text{-}Al_2O_3+3TiB_2$$

From the above thermodynamic analysis, it can be concluded that when the B_2O_3/TiO_2 mole ratio is 0, the combustion results are composed of α-Al_2O_3 and Al_3Ti. With the increase of B_2O_3/TiO_2 mole ratio, the amount of Al_3Ti phase will decrease, and finally as the B_2O_3/TiO_2 mole ratio increases to 1, the Al_3Ti phase will disappear.

3.2 Results and analysis

Fig.3(a) displays that the reaction products in sample A are composed of fine particles and rod-like phase, and Fig.3(b) shows that the reaction products are α-Al_2O_3 and Al_3Ti. Figs.3(c) and (d) are their EDS patterns for the rod-like phase and the particle, respectively, which confirm that the rod-like phase is Al_3Ti and the particle is α-Al_2O_3. Each of Al_3Ti phase can act as an nuclei in the matrix during the solidification

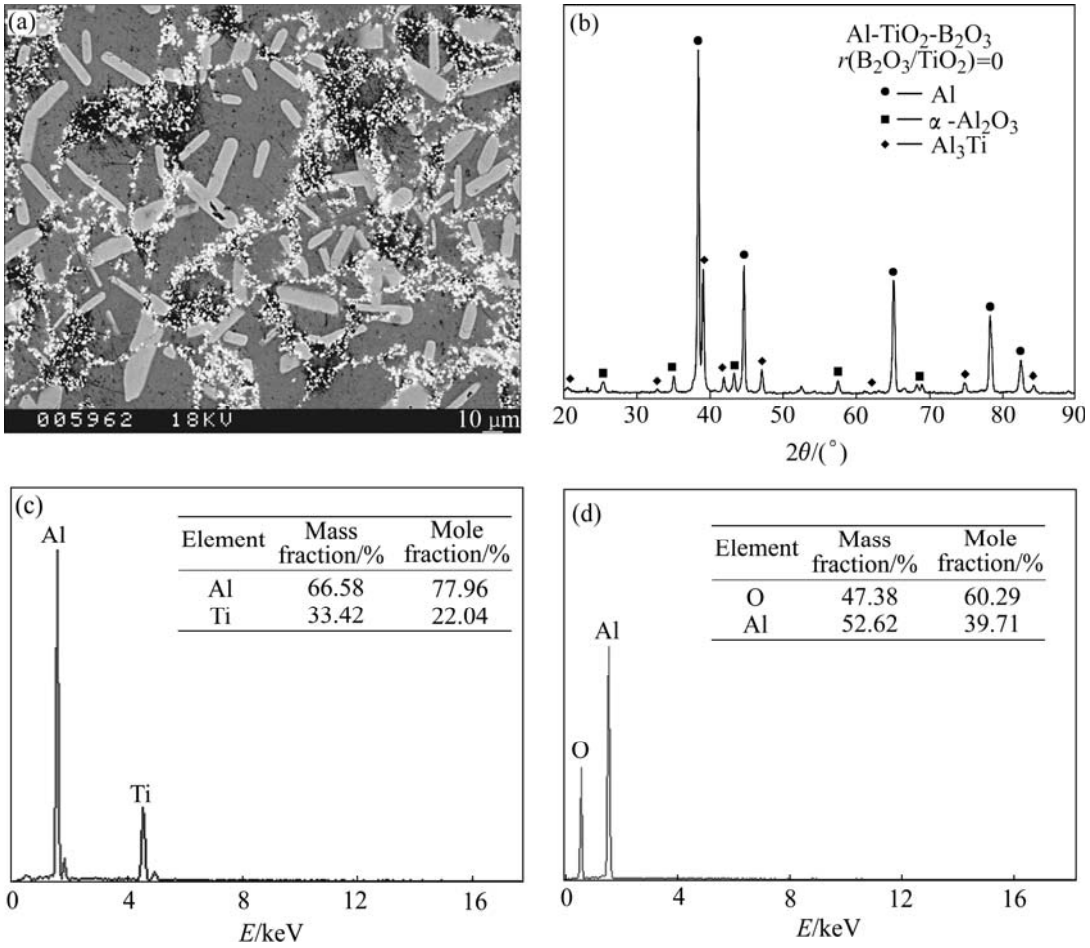


Fig.3 SEM micrograph (a) and XRD pattern (b) of produced sample A as well as EDS patterns (c, d) of rod-like phase and particle, respectively

due to its good orientation relationships within aluminum matrix [11]: ⟨110⟩ $\{112\}_{Al_3Ti}$ //⟨110⟩$\{111\}_{Al}$; ⟨210⟩ $\{112\}_{Al_3Ti}$ //⟨110⟩$\{111\}_{Al}$. The preferential growing direction of the Al_3Ti is ⟨110⟩[12], and then it grows into rod-like of several tens microns in length.

Owing to the small fraction of Al_3Ti phase, it is hard to refine the matrix considerably. The α-Al_2O_3 particles are formed directly from reactions (1) and (2). They segregated on the grain boundaries because of the following three reasons: 1) the size of α-Al_2O_3 particles is 2−3 μm and it is difficult for the α-Al_2O_3 particles to enter the matrix during the solidification; 2) the viscosity of matrix increases quickly due to the reaction temperature decreasing rapidly after combustion; 3) the low wettability between the α-Al_2O_3 and aluminum matrix. The needed outer work for the α-Al_2O_3 particles entering into matrix is reported previously as[13]

$$W=\frac{3\sigma_{lg}(1-\cos\theta)^2}{4R}f_p \tag{10}$$

where W is the outer work; f_P is the particle volume fraction; R is the particle radius; σ_{lg} is the liquid-solid interface energy; θ is the wetting angle. Here θ is 118° [14], therefore W of α-Al_2O_3 particles is very high, which makes α-Al_2O_3 particles hard to enter into Al matrix.

As adding B_2O_3 powders, B_2O_3 powders will be melt at the temperature of 633 K and then enter into the aluminum powders by the capillary force. Reaction (2) will occur at the temperature of about 1 000 K and produce active B atoms. Then the active B will react with active Ti atoms produced by reaction (1) to form TiB_2 particles. When the B_2O_3/TiO_2 mole ratio is 0.5(sample B), the SEM micrograph of the combustion results indicates that the amount of Al_3Ti sticks decreases, as shown in Fig.4(a), which is consistent with the XRD result in Fig.4(c). When the B_2O_3/TiO_2 mole ratio is 1 (sample C), the Al_3Ti phase disappears, as shown in Fig.4(b), and the corresponding XRD spectrum in Fig.4(d) also shows that there is no diffraction peaks of Al_3Ti, which is in agreement with the conclusion of above thermodynamic analysis.

In the Al-TiO_2-B reaction system, YANG et al[15] suggested that B powder can be combined directly with liquid Al to form AlB_{12}, and then AlB_{12} is decomposed as following equation: $AlB_{12}\rightarrow 12[B]+Al$, to form active B and Al. At the same time, TiO_2 powder reacts with Al to produce active Ti. The active B atoms react with Ti atoms to form TiB_2. But in the Al-TiO_2-B_2O_3 reaction system, Al reacts with TiO_2 and B_2O_3 respectively to form active B and active Ti, then the active Ti will be combined with the active B to form thermodynamically steady phase TiB_2, and there are no intermediate phases AlB_{12}. When the B_2O_3/TiO_2 mole ratio is below 1, the active Ti atoms are excess in the reaction, and then the

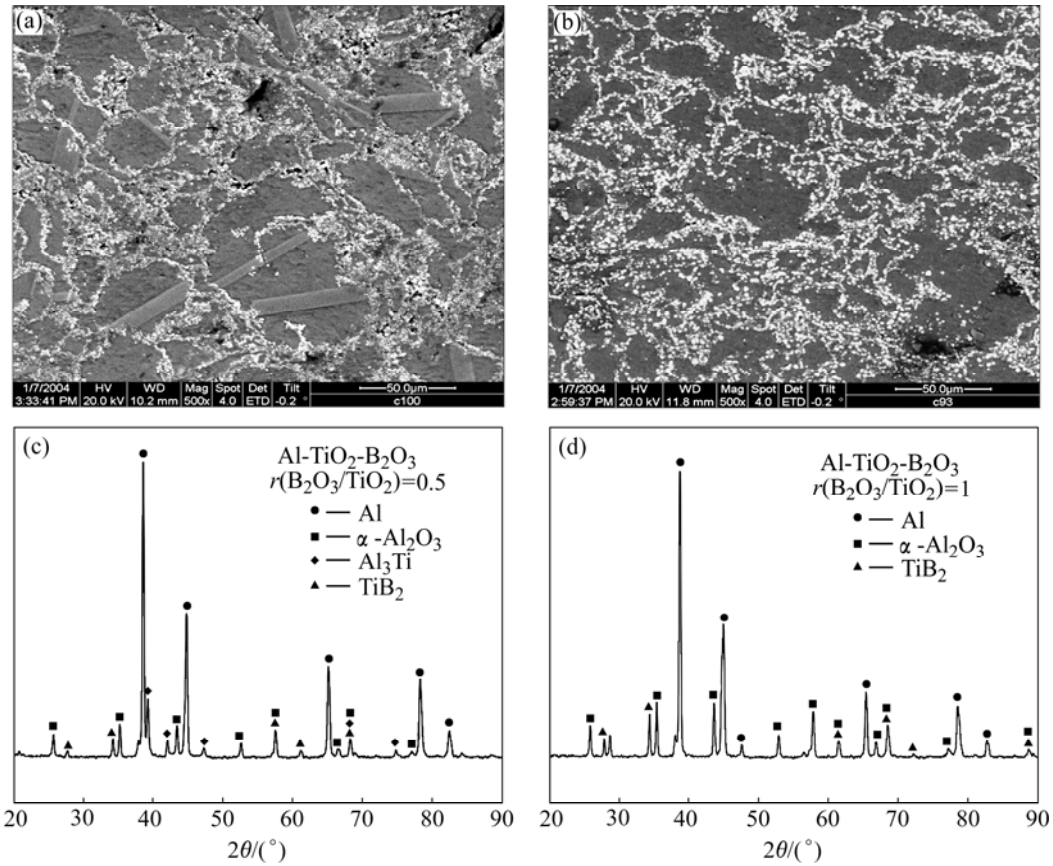
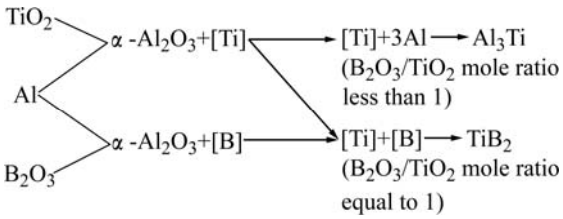


Fig.4 SEM micrographs and XRD patterns of reaction products: (a), (c) Sample A; (b), (d) Sample B

remained Ti atoms will react with Al to form Al_3Ti. With the increase of B_2O_3/TiO_2 mole ratio, the amount of remained Ti atoms decreases. And when the B_2O_3/TiO_2 mole ratio is 1, there is no remained Ti atom to combine with Al to form Al_3Ti. Therefore the reaction route in the Al-TiO_2-B_2O_3 system can be shown as follows:



It can be noted that the SEM micrographs of Al_3Ti and the reaction process of TiB_2 in the Al-TiO_2-B_2O_3 are different from those in the Al-TiO_2-B system. In the Al-TiO_2-B system, when the B/TiO_2 mole ratio is less than 2, the products consist of α-Al_2O_3, Al_3Ti and TiB_2, and firstly B will react with Al to form $Al_{12}B$ and then $Al_{12}B$ will decompose to produce active B. The active B will diffuse to the surfaces of Al_3Ti and react with Al_3Ti to form TiB_2, whereas the active B is not enough to reduce all the Al_3Ti. Therefore, the surfaces of the remained Al_3Ti are not smooth[13]. When the B/TiO_2 mole ratio is increased to 2, the Al_3Ti sticks are reduced entirely and no Al_3Ti is observed in the results. According to the previous analysis, the formation time of TiB_2 is later than that of Al_3Ti, and the surfaces of the remained Al_3Ti are not smooth in the Al-TiO_2-B system. However, in the Al-TiO_2-B_2O_3 system, Al can react with TiO_2 and B_2O_3 simultaneously, and then produce active Ti and active B atoms in the matrix. Therefore they can form TiB_2 directly by diffusion. When the B_2O_3/TiO_2 mole ratio is below 1, the remained Ti atoms will react with Al to form Al_3Ti phase, which is smooth surface as shown in Fig.4(a). Therefore, the formation time of TiB_2 is prior to that of Al_3Ti, and the surfaces of the remained Al_3Ti are smooth in the Al-TiO_2-B_2O_3 system.

4 Conclusions

1) In the Al-TiO_2-B_2O_3 reaction system, when the B_2O_3/TiO_2 mole ratio is below 1, the combustion results are composed of α-Al_2O_3, TiB_2 and Al_3Ti. The α-Al_2O_3 phase is the most stable due to its lowest Gibbs free energy in the products.

2) The α-Al_2O_3 particles can not enter Al-based grains and segregate in the matrix grain boundaries. The Al_3Ti phase distributes uniformly in the matrix. The TiB_2 particles are compatible with the matrix and can become the nuclei of the matrix during the solidification, and as a result, the matrix grains can be refined with uniform distribution of the α-Al_2O_3 particles in the matrix.

3) As the B_2O_3/TiO_2 mole ratio increases, the fraction of Al_3Ti will decrease, and if the ratio reaches 1, the Al_3Ti phase disappears in the composites.

4) In the Al-TiO_2-B_2O_3 reaction system, the active Ti and B produced by reactions (1) and (2) respectively can form TiB_2 directly by diffusion. When the B_2O_3/TiO_2 mole ratio is less than 1, there are still some active Ti atoms remained, and then these active Ti atoms will react with Al to form Al_3Ti phases whose surfaces are smooth.

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