

In-Situ Formation of Reinforcements in Reactive Sintered Aluminum Matrix Composites

Zhongchun Chen, Takenobu Takeda*, Akira Satoh*, Shin-ichi Kikuchi* and Keisuke Ikeda

Department of Materials Processing, School of Engineering, Tohoku University, Sendai 980-8579, Japan

Fax: 81-22-217-7346, e-mail: czc@material.tohoku.ac.jp

*Department of Mechanical Engineering, Faculty of Engineering, Yamagata University, Yonezawa 992-8510, Japan

Aluminum matrix composites reinforced with TiB₂ and Al₂O₃ particles were synthesized via reactive sintering of Al-TiO₂-B powder system. The objective of this work was to clarify the effects of reactive sintering temperature and powder particle size on the formation of reinforcing phases and microstructural evolution. The reduction reaction of TiO₂ by molten Al has been proved to be a stepwise process, and several oxygen deficient titanium oxides could be formed. There existed several transitional phases, such as AlB₂, γ-Al₂O₃, Al₃Ti and oxygen deficient titanium oxides, during the reactive sintering process. As the reinforcements in final composites, Al₂O₃ was formed via a series of aluminothermic reactions, while TiB₂ was generated through solid-solid interfacial reactions. Small sized TiO₂ powder promoted the formation of the reinforcing phases at lower temperatures. Furthermore, the resultant reinforcing particles exhibited smaller sizes in comparison with large sized TiO₂ powder.

Key words: in-situ composites, metal matrix composites, reactive sintering, thermite reaction, particle size

1. INTRODUCTION

Aluminum based metal matrix composites (MMCs) reinforced with rigid ceramic particulates have become more and more attractive for structural applications in aerospace, automotive and transport industries, because of their high specific strength and modulus, good wear resistance as well as ease of processing. In the last decade, various *in situ* techniques, including exothermic dispersion (XD), self-propagating high temperature synthesis (SHS), reactive sintering and reactive gas infiltration [1-6], have been developed to fabricate MMCs with ultrafine reinforcing particulates, which are formed *in situ* by chemical reactions between elements or between elements and compounds.

Reactive sintering of multi-component powder mixture is one of the important routes to fabricate Al based *in situ* MMCs. Since various chemical reactions take place during the reactive sintering process, the composition and microstructure of finished MMCs are quite different from those of the starting materials. It is believed, therefore, that the processing parameters of reactive sintering and the characteristics of raw powders will dominate the formation of the reinforcing phases and, hence, the microstructural development and mechanical properties of the MMCs. Unfortunately, the influence of processing parameters and powder characteristics on the reaction mechanisms, phase evolution and microstructural development during the reactive sintering, which is very important to optimize the *in situ* process and mechanical properties of *in situ* processed MMCs, has not been well understood.

In the present work, Al-TiB₂-Al₂O₃ *in situ* composites were synthesized by reaction sintering of Al-B-TiO₂ powder mixtures. The objective was to clarify the effects of reactive sintering temperature and powder particle size on formation of the reinforcing phases and microstructural evolution of Al based *in situ* MMCs.

2. EXPERIMENTAL PROCEDURE

The raw powders used in this investigation were: aluminum (99.7% purity), boron (99.0%), and TiO₂ (rutile type). The average particle sizes of Al and B were 45μm and 31μm, respectively. Two types of TiO₂ powders with average particle sizes of 2μm (99.0% purity) and 0.5μm (99.9% purity) were used, and they are denoted as TiO₂(A) and TiO₂(B), respectively.

The powders of Al, TiO₂, and B were ball-milled in ethanol for 24 h. The mixing proportion of the powders was determined in accordance with the stoichiometry of the following reaction formula:



Where x represents excess amount of Al, which constitutes the matrix of the final composites. In this work, the Al matrix composites were designed to possess a nominal composition containing 20vol% reinforcements (TiB₂ and Al₂O₃) after complete reactive sintering according to the formula (1).

The mixed powder slurries were dried and then uniaxially compacted with a pressure of 200 MPa. The pressed pellets were heated in vacuum to certain temperature ranging from 700°C to 1000°C for 10 min., followed by cooling to room temperature.

The phase identifications for compacted powder mixtures and reactive sintered samples were performed by X-ray diffraction (XRD) with CuK_α radiation. The microstructures were characterized using scanning electron microscopy (SEM) with an energy dispersive X-ray spectroscopy (EDS).

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction analysis

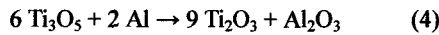
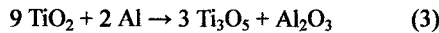
The X-ray diffraction patterns for Al-B-TiO₂(A) samples sintered at different temperatures in the range of 700-1000°C are shown in Fig.1. As a reference, the XRD pattern of the compact of Al, B, and TiO₂ mixed

powder was also included in Fig.1. The pattern (Fig.1(a)) exhibited well-defined peaks of Al and TiO₂. But no distinct peaks of B were detected because of its low density and small content in the mixture. For the sample sintered at 700°C (Fig.1(b)), some small peaks of AlB₂, α-Al₂O₃ and three titanium oxides (Ti₃O₅, Ti₂O₃ and TiO) with lower oxygen concentrations than TiO₂ were identified, along with the strong peaks of TiO₂ and Al. It is evident that the formation of these compounds is the result of the chemical reactions among TiO₂, B, and Al during the reactive sintering.

Obviously, at 700°C (more than the melting point of Al: 660°C), the TiO₂ and B particles are distributed in liquid Al melt. Because of the intimate contacts between TiO₂ particles and Al melt as well as between B particles and Al melt, it is believed that the Al/TiO₂ and Al/B reactions take place easily. According to Al-B phase diagram [7], B reacts with Al at ~660°C in the following way:



With regard to the Al/TiO₂ reactions, the occurrence of three different titanium oxides with a general formula Ti_nO_{2n-1} (n=1, 2, 3) shows that the reduction reaction of TiO₂ is a stepwise process, which is likely to occur in terms of the following sequences:



Since the above aluminothermic reactions (3)-(5) are exothermic processes, these reactions cause the increase in temperature of the Al melt, hence further promoting Al/B, Al/TiO₂, and Al/Ti_nO_{2n-1} reactions.

When the sintering temperature was raised to 800°C, as the thermite reactions proceeded, the intensity of TiO₂ phase was greatly reduced, whereas Ti₂O₃ became one of the main phases. This suggests that the majority of TiO₂ particles have transformed into Ti₂O₃ by reactions (3) and (4), that is,

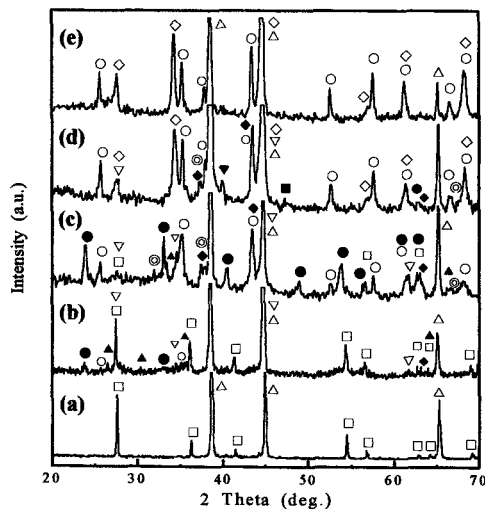
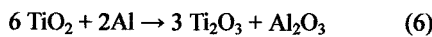


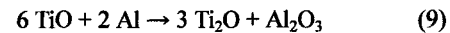
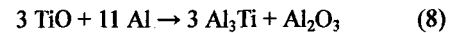
Fig.1 XRD patterns for Al-B-TiO₂(A) samples of (a) unreacted compact, and sintered for 10 min. at (b) 700°C, (c) 800°C, (d) 900°C, and (e) 1000°C. (Δ) Al, (○) α-Al₂O₃, (◇) TiB₂, (□) TiO₂, (▽) AlB₂, (●) Ti₂O₃, (▲) Ti₃O₅, (◆) TiO, (▼) Ti₂O, (◎) γ-Al₂O₃, and (■) Al₃Ti.

It can be seen from Fig.1(c) that a small amount of γ-Al₂O₃ was produced at 800°C. It has been reported [8] that γ-Al₂O₃ can be formed by the interfacial reaction between TiO₂ and Al. Furthermore, γ-Al₂O₃ is not stable in Al and will be readily transformed into more stable α-Al₂O₃ at higher temperatures.

At 900°C, TiO₂ and Ti₂O₃ were consumed almost completely, and TiB₂ phase was confirmed. The occurrence of TiB₂ may result from the following reaction path (7), which is in agreement with the reaction mechanism proposed by Feng and Froyen [6].



Moreover, trace amount of Al₃Ti appeared. Concerning the formation of Al₃Ti, some researchers [5,6] thought to be the result of direct reaction between TiO₂ and molten Al. Because of the stepwise reaction characteristics of TiO₂ as stated before, it seems reasonable to assume that one of the oxygen deficient titanium oxides is involved in the reaction. On the other hand, a peak corresponding to an angle of ~39.9° was observed from Fig.1(d), which is associated with another titanium oxide Ti₂O. The formation of Al₃Ti and Ti₂O phases might be attributed to two superimposed reduction reactions involving TiO and Al via the following reactions:



TiO could be continuously supplied by consuming Ti₂O₃ (reaction (5)).

After sintering at 1000°C, the transitional phases, such as Ti₂O, Al₃Ti and γ-Al₂O₃, disappeared completely. Only those peaks of two expected reinforcing phases, α-Al₂O₃ and TiB₂, were observed in the XRD pattern, in addition to the peaks of Al matrix. The elimination of small amount of Ti₂O and Al₃Ti is considered to be due to the following reactions (10) and (11), respectively.

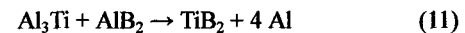
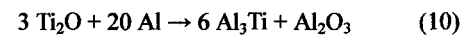


Fig.2 illustrates the XRD spectra for Al-B-TiO₂(B) samples, where small sized TiO₂(B) powder was used. At a sintering temperature of 700°C, the spectrum (Fig.2(a)) was somewhat similar to that of Al-B-TiO₂(A) sample shown in Fig.1(b). Nevertheless, the relative

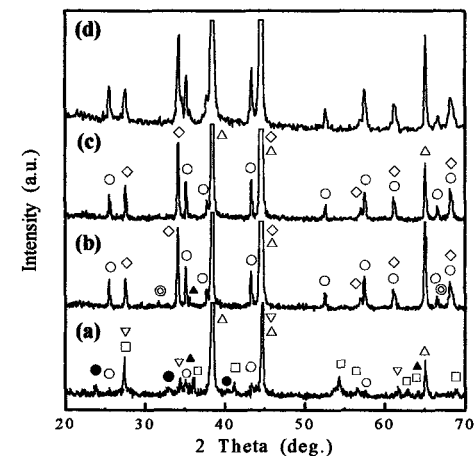


Fig.2 XRD patterns for Al-B-TiO₂(B) samples sintered for 10 min. at (a) 700°C, (b) 800°C, (c) 900°C, and (d) 1000°C. The symbols are the same as those in Fig.1.

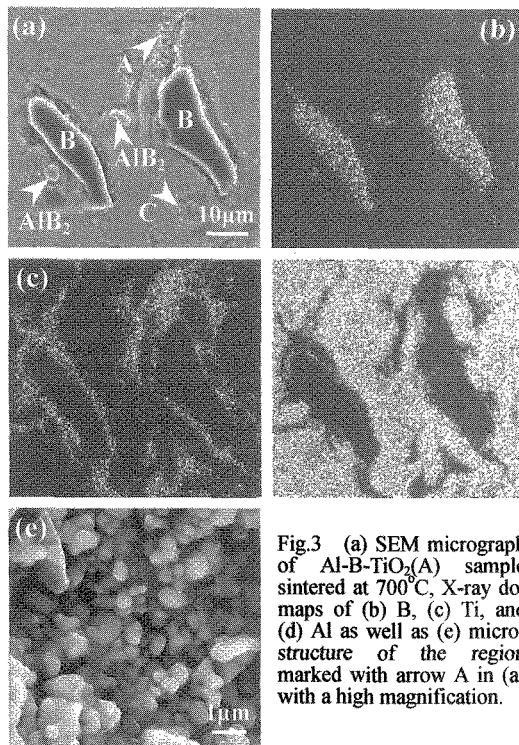


Fig.3 (a) SEM micrograph of Al-B-TiO₂(A) sample sintered at 700°C, X-ray dot maps of (b) B, (c) Ti, and (d) Al as well as (e) microstructure of the region marked with arrow A in (a) with a high magnification.

intensities of the reaction products in Fig.2(a) seem to be higher, compared to those in Fig.1(b). When the temperature reached 800°C, the spectrum consisted primarily of Al, α -Al₂O₃, and TiB₂, with trace amount of γ -Al₂O₃ and Ti₃O₅ remaining. With a further increase in the sintering temperature, for example, at 900°C and 1000°C, the XRD spectra showed almost the same pattern, in which there existed no transitional phases. As a result, the spectra were composed of the peaks corresponding to Al, α -Al₂O₃, and TiB₂ phases.

From the above results, as the reinforcing particulates in final composites, Al₂O₃ can be formed via a series of aluminothermic reactions, while TiB₂ is generated through solid-solid interfacial reactions (Eqs.(7) and (11)). The formation of the latter is dominated to a large extent by AIB₂. When a finer TiO₂(B) powder is used as one of the starting powders, the formation of TiB₂ and Al₂O₃ reinforcing phases in Al matrix is shifted to a lower temperature. The main reason for this should be that small sized TiO₂ powder can increase the diffusion and reaction rates due to large contact area with surrounding molten Al. In addition, the exothermic process related to aluminothermic reactions further promotes the diffusions and reactions as well.

3.2 Microstructural development

The microstructures of an Al-B-TiO₂(A) sample sintered at 700°C are shown in Fig.3. Although B is difficult to be detected by XRD as stated previously, some larger particles, identified to be B by EDS, were easily observed by SEM (Fig.3(a)). It was seen from the X-ray dot map of Ti (Fig.3(c)) that, the distribution of Ti was not homogeneous in the Al matrix. There were higher Ti concentrations around B particles, or in some places which were adjacent to B particles (such as the region marked with an arrow A in Fig.3(a)) or were in isolated regions within the matrix (marked with an arrow

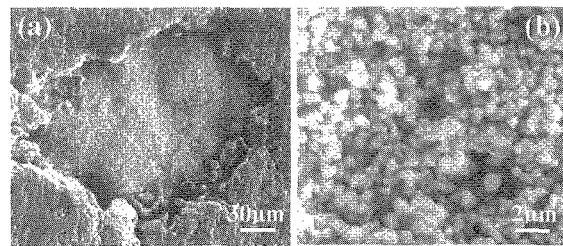


Fig.4 Microstructures of Al-B-TiO₂(A) sample sintered at 800°C. (a) A low magnification, and (b) a magnified micrograph for the region in the middle part in (a).

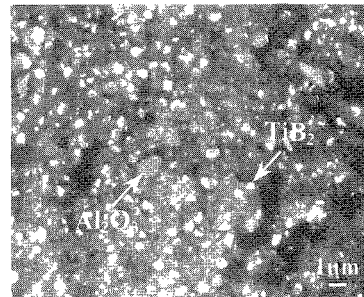


Fig.5 Microstructure of Al-B-TiO₂(A) sample sintered at 1000°C. TiB₂ and Al₂O₃ particulates were dispersed in Al matrix homogeneously.

C). This reveals that the particles of the initial TiO₂ and/or Ti_nO_{2n-1} generated by TiO₂/Al reactions tend to come together, either on the surfaces of B particles or in some isolated regions. Fig.3(e) gives an example showing the microstructure of the region marked with the arrow A in Fig.3(a). A lot of small particles, presumably consisting of TiO₂ and/or oxygen deficient titanium oxides Ti_nO_{2n-1}, were gathered together, in order to reduce interfacial energy.

As shown in Fig.3(a), the original finer B particles appear to react with Al easily and, thus resulting in the formation of AIB₂. On the contrary, for larger sized B particles, the agglomeration of large number of particles on their surfaces impedes the diffusion of B and Al. As a consequence, a higher sintering temperature or long holding time may be required for forming AIB₂.

As the sintering temperature increases, the chemical reactions (2)-(5) proceed rapidly. At 800°C, it is difficult to find the presence of B particles. The microstructural examinations showed that, however, there existed a lot of isolated regions with sizes of 100-200 μ m in the sample, an example is shown in Fig.4(a). An SEM micrograph with a high magnification (Fig.4(b)) revealed that the region involved a large number of small particulates ($\leq 1\mu$ m). The EDS analysis showed that there were high Ti and low Al concentrations in these particulate agglomeration regions. Accordingly, from the XRD results, these particulates are primarily related to Ti₂O₃, with some Al₂O₃, although it is difficult to distinguish Ti₂O₃ from other titanium oxides by EDS due to their similar compositions.

Whether the particulates formed *in situ* disperse or agglomerate in molten Al medium depends on the surface energy of these particulates and particulate/Al interfacial energy. The particulate agglomeration shown in Fig.4 is obviously the result of an energy decrease. In the meantime, the TiO₂(A) powder has a broader particle

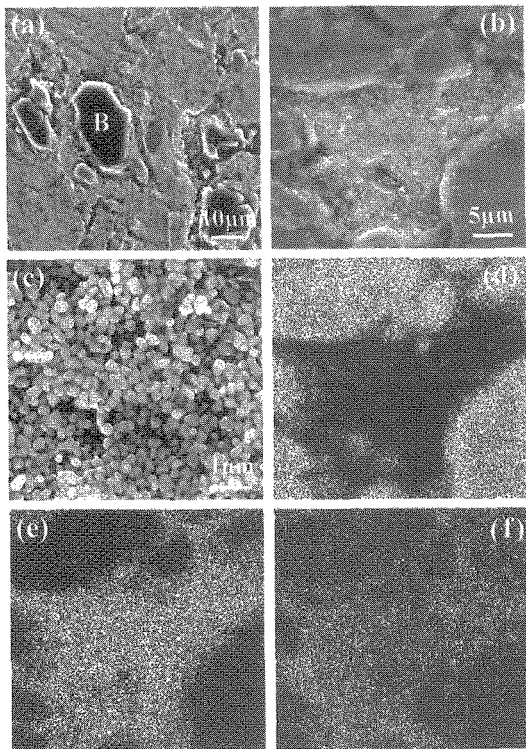


Fig.6 (a) (b) Microstructures of Al-B-TiO₂(B) sample sintered at 700°C, (c) a magnified micrograph for the region in the middle part in (b), and X-ray dot maps of (d) Al, (e) Ti, and (f) O.

size distribution and a larger average particle size. The presence of some large TiO₂ particles gives rise to the formation of numerous Ti₂O₃ and Al₂O₃ particulates in the sites of the original TiO₂ particles. Meanwhile, a short holding time (10min.) and low temperature (800°C) cause the diffusion or movement of the particulates towards the Al melt to be difficult. Consequently, the particulate agglomeration occurs easily, especially in the sites of large TiO₂ particles.

With the increase in sintering temperature, the number of the particulate agglomeration regions decreases and their sizes become small. At 900°C, the average size of particulate agglomeration regions (~25µm) was much smaller than that at 800°C. This is attributed to more rapid diffusion and migration of the particulates at a higher temperature. Besides, a lower viscosity of the Al melt at a higher temperature is also beneficial to the migration of the particulates.

When the reactive sintering was performed at 1000°C, no apparent particulate agglomeration was observed. A typical microstructure for the composite obtained by sintering at 1000°C is shown in Fig.5. Small TiB₂ and Al₂O₃ particulates with sizes of ≤1µm were dispersed in the Al matrix homogeneously.

When small sized TiO₂(B) powder was used, a microstructural feature similar to Fig.3(a) was confirmed for a sample sintered at 700°C (Fig.6(a)). Moreover, a particulate agglomeration region with a size of ~20µm, which was much smaller than that shown in Fig.4(a), was observed (Fig.6(b)). As shown in Fig.6(c), a large number of small particulates with an average size of ~260nm were gathered together. The X-ray maps of

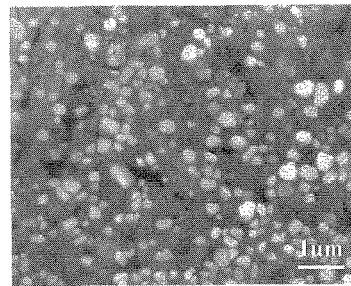


Fig.7 A representative microstructure of Al-B-TiO₂(B) sample sintered at 1000°C. The reinforcing particulates with sizes of ≤0.5µm were dispersed in Al matrix.

elements showed that the resultant particulates mainly contained Ti and O, showing to be titanium oxides. It has been noted that no evident particulate agglomeration was observed for Al-B-TiO₂(B) samples sintered in the range of 800-1000°C. Fig.7 shows an example of the microstructure of an Al-B-TiO₂(B) sample processed at 1000°C. Both TiB₂ and Al₂O₃ particulates were distributed in the Al matrix. The sizes of the particulates were less than 0.5µm, smaller than those when coarser TiO₂(A) powder was used.

4. CONCLUSIONS

(1) Under the conditions of the current investigation, the reduction reaction of TiO₂ by molten Al has been proved to be a stepwise process. Four oxygen deficient titanium oxides (Ti₃O₅, Ti₂O₃, TiO, and Ti₂O) could be formed, and Ti₂O₃ seems to be a main intermediate reaction phase.

(2) There existed several transitional phases, such as AlB₂, γ-Al₂O₃, Al₃Ti and oxygen deficient titanium oxides, during the reactive sintering process of Al-TiO₂-B powder mixtures.

(3) As the reinforcing particulates in final composites, Al₂O₃ was formed via a series of aluminothermic reactions, while TiB₂ was generated through solid-solid interfacial reactions.

(4) The formation of TiB₂ and Al₂O₃ reinforcing phases in Al matrix could be shifted to a lower temperature, when a finer TiO₂ powder was used as one of the starting powders. Furthermore, the resultant reinforcing particles exhibited smaller sizes, compared to large sized TiO₂ powder.

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