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Phase Reactions of Al-Ti-B Ternary and Al-Ti-B-O Quaternary Systems for Al-based Metal Matrix Composites

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In order to fabricate Al-base in-situ metal matrix composites (MMCs) with strengthening dispersions such as TiB_2, phase reactions in the Al-Ti-B ternary system and Al-Ti-B-O quaternary system were investigated and the phase reactions were summarized. Especially, basic phase reactions of the Al-B, Al-Ti, Ti-B binary and the Al-B-Ti ternary system were precisely investigated by differential scanning calorimetry (DSC) up to 1400°C in Ar using mixtures of Al, Ti, B, Al_3Ti, Al_2B, TiO_2 and B_2O_3 powders. Besides, the products formed during DSC measurements were identified by θ-2θ X-ray diffraction analysis at room temperature. It is confirmed that TiB_2 is hardly formed by a direct reaction between Ti and B under the thermal conditions: TiB_2 is judged to be formed at around 1300°C. In the ternary system TiB_2 is formed by the reaction of $AlB_2+Al_3Ti \rightarrow TiB_2+4Al$, and this reaction is evaluated to be the key reaction to form Al/TiB_2 in-situ MMCs. Then, it was understood that a brittle phase Al_3Ti easily remained in the Al-Ti-B system when Al content is less than 57.1mol% (=27.9vol%TiB_2). Besides, the phase reactions in the $Al-B_2O_3$ and $Al-TiO_2$ were also described.

Keywords: *Phase reaction, Al-Ti-B, Al-Ti-B-O, Metal Matrix Composite, TiB_2, Al_3Ti, B_2O_3, TiO_2*

1. Introduction

Aluminum-based metal matrix composites (MMCs) with ceramic reinforcement are fascinating light-weight structural materials equipping with high toughness due to Al matrix and high stiffness and superior heat resistance due to ceramic dispersoids. Several kinds of Al-based MMCs have been reported which contain Al_2O_3 [1], B_4C [2], SiC [3] and TiC [4], for example. In this study, titanium diboride TiB_2 and alumina Al_2O_3 are focused as strengtheners. Besides, several synthesis techniques for the fabrication of $Al-TiB_2$ MMCs have been also reported such as a stir casting method [5], a mechanical alloying method [6] and a combustion reaction [7, 8]. In this paper a reactive powder processing was employed which is a new potentially cost-effective route to fabricate particulate reinforced MMCs [9]. As for such in-situ MMCs, phase reactions and phase constitution of final products are important and desirable microstructures should be obtained by controlling the reactions. The equilibrium phase diagram of the Al-B-Ti has been reported by Witusiewicz et al. [10] and summarized by Raghavan [11], and the isothermal ternary phase diagram at 1000°C is presented in Figure 1. By judging from the phase diagram, two phase MMCs composed of Al and TiB_2 should be made at the tie-line compositions between Al and TiB_2. However, unstable intermediate compounds are easily formed during synthesis in some case and undesirable products remain in final products [12-14]. The undesirable product in the Al-B-Ti system is an intermetallic compound Al_3Ti which is soft and brittle in nature [15]. When Al_3Ti remained in the Al/TiB_2 MMCs, the ductility was reported to be largely degraded to be 68% loss, for example [5]. The presence of Al_3Ti is partially because

Al_3Ti is formed directly by the reaction between Al and Ti prior to the formation of TiB_2, since the direct reaction between Ti and B hardly occurs at the temperature below 1200°C [7].

Al/TiB_2 MMCs can be fabricated not only by using elemental powders of Al, B and Ti but also by using Al-, B- and Ti-based compounds and oxides. Wang et al. have reported the synthesis from K_2TiF_6, KBF_4 and molten Al [14], and Taneoka et al. have reported the synthesis using the systems of Al-TiO_2-B and Al-TiO_2-B_2O_3 [16]. Oxides are suitable stating materials from the viewpoint of production cost. Then, in order to fabricate desirable Al-based MMCs without remaining such undesirable intermediate products, phase reactions of the Al-Ti-B ternary system and the Al-Ti-B-O quaternary systems were precisely investigated for the development of Al/TiB_2-based MMCs. This paper summarizes the phase reactions of the Al-B-Ti and Al-B-O-Ti systems where some reactions have been described for the AlB_2-Al_3Ti system [17] and the Al-B-TiO_2 system [18] in addition to high-temperature mechanical properties.

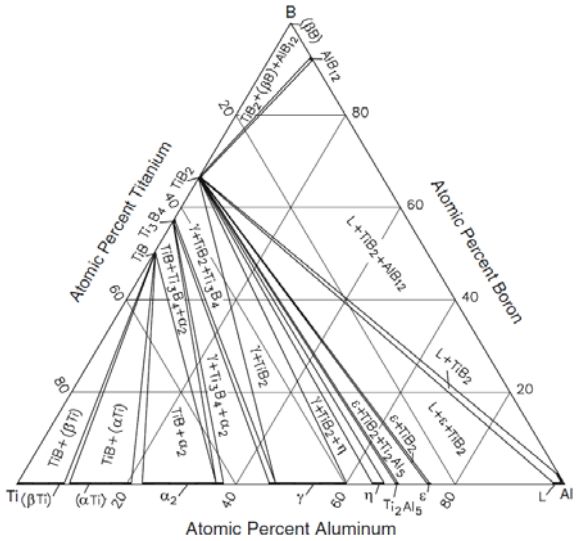

Figure 1 Al-B-Ti computed isothermal section at 1000°C [10, 11].

2. Phase reactions

Expected phase reactions appeared in the ternary and quaternary system are shown in Figure 2. As previously described, since TiB_2 is hardly synthesized by the direct reaction from Ti and B [7], TiB_2 is supposed to be formed by a two-step reaction in the Al-B-Ti ternary system and the sequence is as follows [17].

First step: $Al + 2B \rightarrow AlB_2$ (1)

$3Al + Ti \rightarrow Al_3Ti$ (2)

Second step: $AlB_2 + Al_3Ti \rightarrow 4Al + TiB_2$ (3)

Total reaction: $(4+x)Al + 2B + Ti \rightarrow (4+x)Al + TiB_2$ (x>0) (4)

Based on the chemical reactions, Al content should be larger than 57.1mol%Al (= $Al_4B_4Ti_1$, x=0) if the synthesis of TiB_2 is perfectly done. If the Al concentration is smaller than the critical composition ($Al_4B_4Ti_1$), the intermediate phase Al_3Ti will remain. The critical composition corresponds to Al-27.9vol%TiB_2. Therefore, Al-based MMCs with higher volume fraction of TiB_2 cannot be fabricated by in-situ synthesis, even though Al/TiB_2 two phases are equilibrated in the phase diagram in Fig. 1.

In the case of the quaternary system, fundamental reactions expected are as follow.

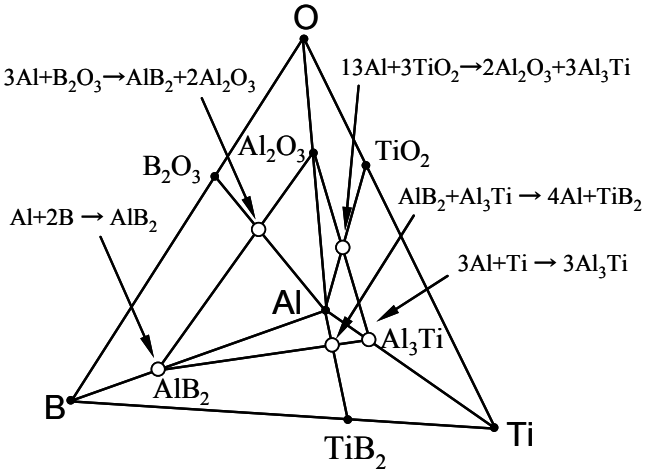

Figure 2 Reactive processes expected in the Al-B-O-Ti quaternary system.

Al_2B formation: $3Al + B_2O_3 \rightarrow Al_2O_3 + AlB_2$ (5)

Al_3Ti formation: $13Al + 3TiO_2 \rightarrow 2Al_2O_3 + 6Al_3Ti$ (6)

The products of AlB_2 formed in Eq.(5) and/or Al_3Ti in Eq.(6) are provided to make TiB_2 in Eq.(3). Therefore, these phase reactions were experimentally clarified.

3. Experimental procedure

Specimen compositions were listed in Table 1. The starting powder materials were Al (99.7% purity, 2-3μm), B (99.5%, <38μm), Ti (99.5%, <40μm), AlB_2 (99%, <44μm), Al_3Ti (>99%, <44μm), B_2O_3 (99.9%, 1-2μm) and TiO_2 (99.9%, <2μm). These powders were mixed by a planetary boll-milling machine (Fritsch Pulverisette 6) in vacuum with alumina balls for 5-8hrs in total with or without methanol. During mixing, temperature was controlled not to be raised over 80°C by stopping the machine. The mixed powders were dried in an oven at 80°C for 2hrs. Then, cold isostatic pressed under 5000atm for 5min was carried out and cylindrical green compacts were obtained. In order to clarify the phase reaction, differential scanning calorimetry (DSC, Netzsch STA449 Jupiter) was also carried out in Ar for the mixed powders. The heating/cooling rate was 10°C/min and high purity alumina crucibles were used. In order to clarify the phase reaction detected by DSC, θ-2θ X-ray diffraction analysis (XRD, PANalytical X'Pert Galaxy) was carried out for the specimens after DSC. The measuring temperature was room temperature (RT) and CuKα radiation was used where the scan angles were from 20° to 120° in 2θ. Besides, the green compacts were heat-treated below and above the reaction temperature for 30min and XRD analysis were done similarly.

Table 1 Specimen compositions and expected reactions

Specimens	Compositions	Reactions expected		
Ti-2B	Ti:B=1:2	$Ti + 2B \rightarrow TiB_2$	one step	
Al-2B	Al:B=1:2	$Al + 2B \rightarrow AlB_2$	one step	Eq.(1)
3Al-Ti	Al:Ti=3:1	$3Al + Ti \rightarrow Al_3Ti$	one step	Eq.(2)
AlB_2-Al_3Ti	AlB_2:Al_3Ti=1:1	$AlB_2 + Al_3Ti \rightarrow 4Al + TiB_2$	one step	Eq.(3)
Al-B_2O_3	Al:B_2O_3=3:1	$3Al + B_2O_3 \rightarrow Al_2O_3 + AlB_2$	one step	Eq.(5)
Al-TiO_2	Al:TiO_2=13:3	$13Al + 3TiO_2 \rightarrow 2Al_2O_3 + 6Al_3Ti$	one step	Eq.(6)
Al-Ti-B	A:Ti:B=4.6:1:2 (Al-25vol%TiB_2)	$Al + 2B \rightarrow AlB_2$ $3Al + Ti \rightarrow Al_3Ti$ $AlB_2 + Al_3Ti \rightarrow 4Al + TiB_2$	two step	Eqs.(1)-(3)

4. Results and discussion

Figure 3 shows DSC curves of Ti-2B, Al-2B, Al-3Ti, AlB_2-Al_3Ti, Al-B_2O_3 andAl-TiO_2. Besides, corresponding XRD profiles are shown in Figure 4 for Ti-2B heat-treated at (a) 1000˚C and (b) 1400˚C, Al-2B heat-treated at (c) 900˚C and (d) 1200˚C, (e) Al-3Ti heat-treated at 1200˚C and (f) AlB_2-Al_3Ti heat-treated at 1200˚C.

In the case of Ti-2B, a exothermic reaction was found at around 1300˚C by DSC. XRD analysis revealed that very small amount of Ti-B products were formed at 1000˚C, and that TiB2 was the major constituent after the heat treatment at at 1400˚C for 30min. Then, the reaction seen in DSC is evaluated to be $Ti+2B \rightarrow TiB_2$. However, an intermediate phase TiB also remained after the heat-treatment. Then, the direct reaction from Ti and B hardly occurs in the Ti-B binary system. It should be noted that, although the allotropic phase transition from α (hcp) to β (bcc) should be taken place at 885˚C for Ti powder, clear endothermic heat flow was not detected.

In the case of Al-B binary system, an endothermic heat was observed near 660˚C. This is the melting of Al. Then, an exothermic heat existed just above the melting. This is the formation of AlB_2 by the XRD profile. In addition, an endothermic heat was confirmed at around 1050˚C. According to the Al-B binary phase diagram [19], this reaction is the peritectic phase decomposition from $AlB_2 \rightarrow Al+AlB_{12}$. The formation of AlB_{12} was also confirmed by XRD (Fig.4(d))

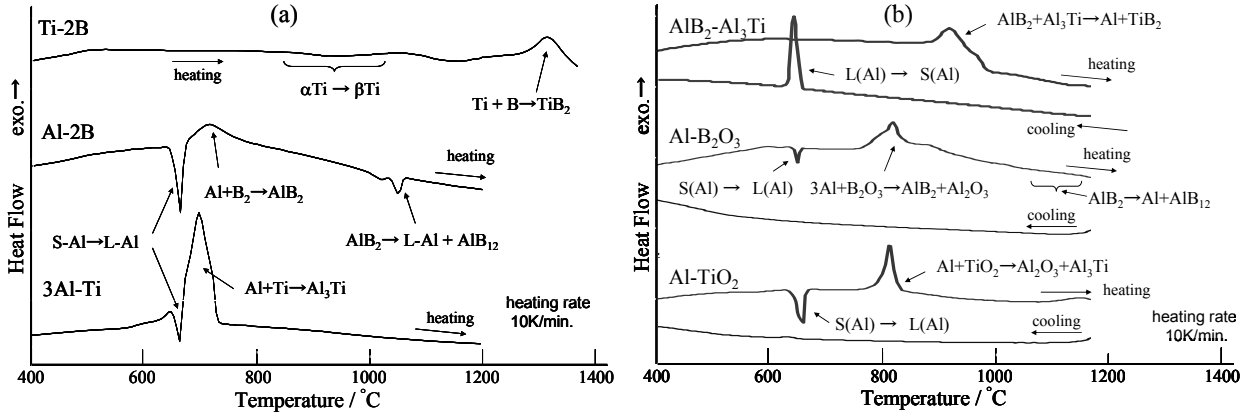

Figure 3 DSC curves of (a) Al-2B, 3Al-Ti and Ti-2B, and (b) AlB_2-Al_3Ti, Al-B_2O_3 and Al-TiO_2. "S" and "L" stand for "solid" and "liquid", respectively for the case of Al.

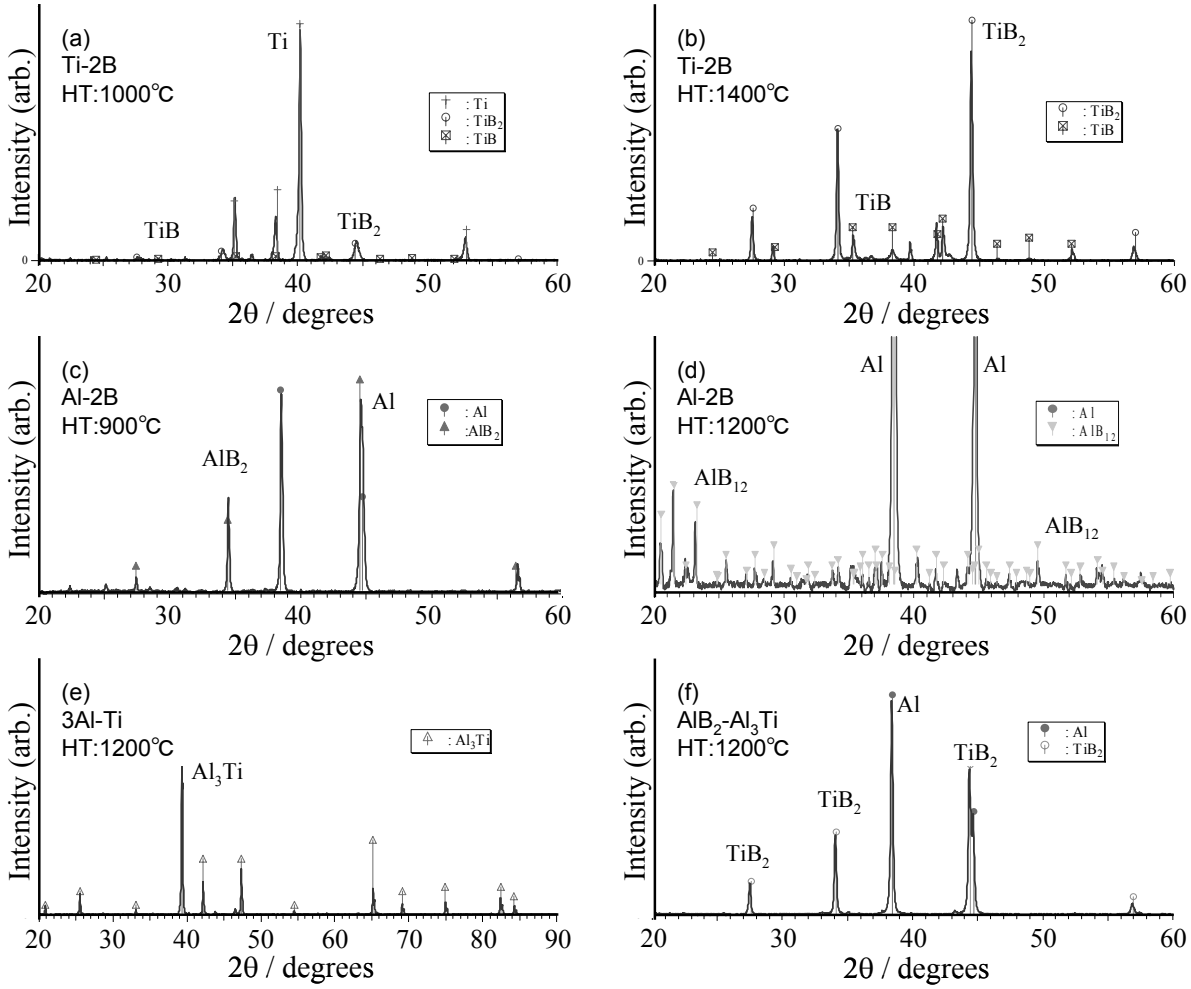

Figure 4 XRD profiles of (a) Ti-2B heat-treated at 1000˚C, (b) Ti-2B heat-treated at 1400˚C, (c) Al-2B heat-treated at 900˚C, (d) Al-2B heat-treated at 1200˚C, (e) 3Al-Ti heat-treated at 1200˚C and (f) AlB_2-Al_3Ti heat-treated at 1200˚C.

In 3Al-Ti, small endothermic heat at 660˚C followed by large exothermic heat was observed. XRD revealed that Al_3Ti single phase was formed after the heat-treatment at 1200˚C for 30min. Then, this reaction is identified to be $3Al+Ti \rightarrow Al_3Ti$.

In the case of AlB_2-Al_3Ti, an exothermic heat was observed at 900˚C. In the cooling curve, one exothermic heat was obtained at 650˚C. This corresponds to the solidification temperature of Al. XRD in Fig.4 (f) revealed that Al and TiB_2 two phases existed after the heat-treatment at 1200˚C. The reaction temperature of 900˚C is, thus, the reaction start temperature of $AlB_2+Al_3Ti \rightarrow 4Al+TiB_2$, and the reaction temperature is much lower than 1300˚C in the Ti-B binary system. Therefore, this reaction is the key reaction to form Al/TiB_2 in-situ MMCs. For the complete progress of the TiB_2 formation, the minimum Al content required is 57.1mol% (=4Al-2B-Ti). This corresponds to Al-27.9vol%TiB_2 at the critical composition. If the Al content is smaller than 57.1mol%, it is understood that at a brittle phase Al_3Ti easily remains. Therefore, the volume fraction of TiB_2 should be designed to be lower than 27.9vol% in the Al-TiB_2 in-situ MMCs.

In both Al-B_2O_3 and Al-TiO_2, exothermic reactions existed at 800˚C. XRD revealed that the reaction was $3Al + B_2O_3 \rightarrow AlB_2 + Al_2O_3$ and $Al + TiO_2 \rightarrow Al_2O_3 + Al_3Ti$. Therefore, it is quite acceptable that a similar chemical reaction from AlB_2+Al_3Ti to $4Al+TiB_2$ must occur after when AlB_2 and Al_3Ti are formed in the Al-B-O-Ti quaternary system.

In order to form Al-TiB_2 in-situ MMCs directly from a mixture of elemental powders, the two-step reaction was controlled by designing a heat treatment condition. Figure 5 shows DSC curves and the specimen temperature of Al-Ti-B with Al-rich composition. The second reaction of $AlB_2 + Al_3Ti \rightarrow 4Al + TiB_2$ was expected to be progressed during holding at 1000˚C for 60min. During heating, two key reactions of $Al+3Ti \rightarrow Al_3Ti$ and $Al+2B \rightarrow AlB_2$ were detected. And in the cooling process a large exothermic heat corresponding to Al solidification was confirmed. After the heat treatment, XRD revealed that this specimen was composed of Al and TiB_2 two phases. Figure 7 shows a SEM micrograph of Al-Ti-B after the heat treatment similar to Fig.5. The cuboidal particles were TiB22 with the diameter being less than 1μm. besides, the composite was dense

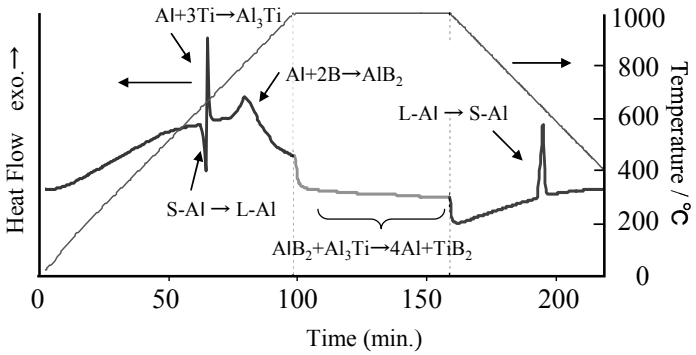

Figure 5 DSC curve and temperature of Al-Ti-B as a function of time.

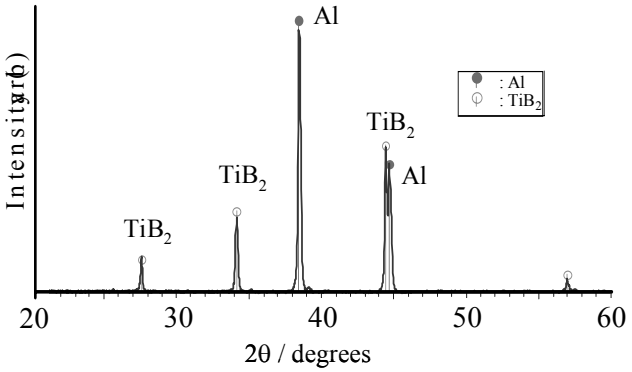

Figure 6 XRD profile of Al-Ti-B after the DSC measurement in Fig.5.

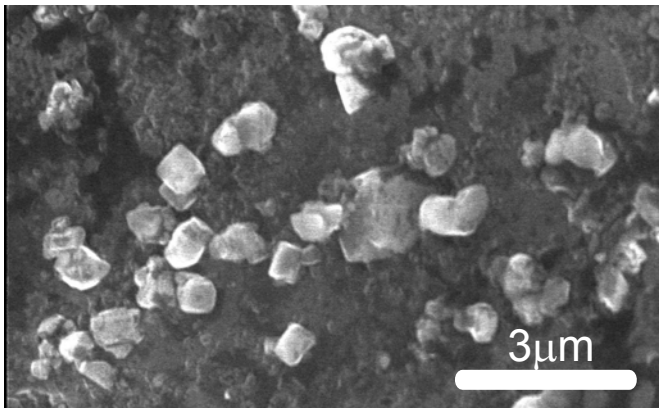

Figure 7 SEM micrograph of Al-Ti-B.

with matrix Al and precipitates TiB_2.

Therefore, it is concluded that the formation of AlB_2 and Al_3Ti and the reaction of $AlB_2 + Al_3Ti \rightarrow 4Al + TiB_2$ are important rate controlling factors for the synthesis of Al-TiB_2 in-situ composites.

Conclusions

1. The reaction temperature of $Ti+ 2B \rightarrow TiB_2$ was about 1300˚C, and TiB intermediate phase still remained after the heat treatment at 1400˚C for 30min.
2. The phase reaction of $Al + 2B \rightarrow AlB_2$ was recognized at about 700˚C. The AlB_2 was discomposed at about 1050˚C due to the peritectic reaction of $AlB_2 \rightarrow (Al)+AlB_{12}$.
3. The phase reaction of $3Al + Ti \rightarrow Al_3Ti$ is easily taken place just after melting of Al.
4. The key reaction to form Al-TiB_2 in-situ MMCs is $AlB_2 + Al_3Ti \rightarrow 4Al + TiB_2$, and this reaction was activated at about 900˚C. Based on the chemical reactions, the maximum fraction of TiB_2 is evaluated to be 27.9vol%.
5. Both the two reactions of $3Al + B_2O_3 \rightarrow Al_2O_3 + AlB_2$ and $13Al + 3TiO_2 \rightarrow 2Al_2O_3 + 6Al_3Ti$ were progressed at about 800˚C.

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