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 TiB₂, 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, Al₃Ti, Al₂B, TiO₂ and B₂O₃ powders. Besides, the products formed during DSC measurements were identified by θ-2θ X-ray diffraction analysis at room temperature. It is confirmed that TiB₂ is hardly formed by a direct reaction between Ti and B under the thermal conditions: TiB₂ is judged to be formed at around 1300°C. In the ternary system TiB₂ is formed by the reaction of AlB₂+Al₃Ti → TiB₂+4Al, and this reaction is evaluated to be the key reaction to form Al/TiB₂ in-situ MMCs. Then, it was understood that a brittle phase Al₃Ti easily remained in the Al-Ti-B system when Al content is less than 57.1mol% (=27.9vol% TiB₂). Besides, the phase reactions in the Al-B₂O₃ and Al-TiO₂ were also described.

Keywords: Phase reaction, Al-Ti-B, Al-Ti-B-O, Metal Matrix Composite, TiB₂, Al₃Ti, B₂O₃, TiO₂

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 Al₂O₃ [1], B₄C [2], SiC [3] and TiC [4], for example. In this study, titanium diboride TiB₂ and alumina Al₂O₃ are focused as strengtheners. Besides, several synthesis techniques for the fabrication of Al-TiB₂ 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 TiB₂ should be made at the tie-line compositions between Al and TiB₂. 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 Al₃Ti which is soft and brittle in nature [15]. When Al₃Ti remained in the Al/TiB₂ MMCs, the ductility was reported to be largely degraded to be 68% loss, for example [5]. The presence of Al₃Ti is partially because
Al$_3$Ti 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$_2$TiF$_6$, 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$_2$O$_3$ [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$_3$Ti system [17] and the Al-B-TiO$_2$ system [18] in addition to high-temperature mechanical properties.

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:  
\[ \text{Al} + 2\text{B} \rightarrow \text{AlB}_2 \]  
\[ 3\text{Al} \rightarrow \text{Al}_3\text{Ti} \]  

Second step:  
\[ \text{AlB}_2 + \text{Al}_3\text{Ti} \rightarrow 4\text{Al} + \text{TiB}_2 \]  

Total reaction:  
\[ (4+x)\text{Al} + 2\text{B} + \text{Ti} \rightarrow (4+x)\text{Al} + \text{TiB}_2 \quad (x>0) \]  

Based on the chemical reactions, Al content should be larger than 57.1mol%Al (= Al$_{4}$B$_4$Ti$_1$, \(x=0\)) if the synthesis of TiB$_2$ is perfectly done. If the Al concentration is smaller than the critical composition (Al$_{4}$B$_4$Ti$_1$), the intermediate phase Al$_3$Ti 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.
Al$_2$B formation: \[ 3\text{Al} + \text{B}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + \text{AlB}_2 \] (5)

Al$_3$Ti formation: \[ 13\text{Al} + 3\text{TiO}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 6\text{Al}_3\text{Ti} \] (6)

The products of AlB$_2$ formed in Eq.(5) and/or Al$_3$Ti 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$_3$Ti (>99%, <44μm), B$_2$O$_3$ (99.9%, 1-2μm) and TiO$_2$ (99.9%, <2μm). These powders were mixed by a planetary ball-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, 0-20 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>
<thead>
<tr>
<th>Specimens</th>
<th>Compositions</th>
<th>Reactions expected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-2B</td>
<td>Ti:B=1:2</td>
<td>Ti + 2B → TiB$_2$</td>
</tr>
<tr>
<td>Al-2B</td>
<td>Al:B=1:2</td>
<td>Al + 2B → AlB$_2$</td>
</tr>
<tr>
<td>3Al-Ti</td>
<td>Al:Ti=3:1</td>
<td>3Al + Ti → Al$_3$Ti</td>
</tr>
<tr>
<td>AlB$_2$-Al$_3$Ti</td>
<td>AlB$_2$:Al$_3$Ti=1:1</td>
<td>AlB$_2$ + Al$_3$Ti → 4Al + TiB$_2$</td>
</tr>
<tr>
<td>Al-B$_2$O$_3$</td>
<td>Al:$B_2$O$_3$=3:1</td>
<td>3Al + B$_2$O$_3$ → Al$_2$O$_3$ + AlB$_2$</td>
</tr>
<tr>
<td>Al-TiO$_2$</td>
<td>Al:TiO$_2$=13:3</td>
<td>13Al + 3TiO$_2$ → 2Al$_2$O$_3$ + 6Al$_3$Ti</td>
</tr>
</tbody>
</table>
| Al-Ti-B   | A:Ti:B=4.6:1:2 (Al-25vol%TiB$_2$) | Al + 2B → AlB$_2$  
 3Al + Ti → Al$_3$Ti  
 AlB$_2$ + Al$_3$Ti → 4Al + TiB$_2$ |

4. Results and discussion

Figure 3 shows DSC curves of Ti-2B, Al-2B, Al-3Ti, AlB$_2$-Al$_3$Ti, Al-B$_2$O$_3$ and Al-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$_3$Ti 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 TiB$_2$ 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→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 allotrophic 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 AlB₂ 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 AlB₂→Al+AlB₁₂. The formation of AlB₁₂ was also confirmed by XRD (Fig.4(d)).

Figure 3 DSC curves of (a) Al-2B, 3Al-Ti and Ti-2B, and (b) AlB₂-Al₃Ti, Al-B₂O₃ and Al-TiO₂. "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) AlB₂-Al₃Ti heat-treated at 1200°C.
In 3Al-Ti, small endothermic heat at 660°C followed by large exothermic heat was observed. XRD revealed that Al₃Ti single phase was formed after the heat-treatment at 1200°C for 30min. Then, this reaction is identified to be 3Al+Ti→Al₃Ti.

In the case of AlB₂-Al₃Ti, 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 revealed that Al and TiB₂ two phases existed after the heat-treatment at 1200°C. The reaction temperature of 900°C is, thus, the reaction start temperature of AlB₂+Al₃Ti→4Al+TiB₂, 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/TiB₂ in-situ MMCs. For the complete progress of the TiB₂ formation, the minimum Al content required is 57.1mol% (=4Al-2B-Ti). This corresponds to Al-27.9vol%TiB₂ at the critical composition. If the Al content is smaller than 57.1mol%, it is understood that at a brittle phase Al₃Ti easily remains. Therefore, the volume fraction of TiB₂ should be designed to be lower than 27.9vol% in the Al-TiB₂ in-situ MMCs.

In both Al-B₂O₃ and Al-TiO₂, exothermic reactions existed at 800°C. XRD revealed that the reaction was 3Al + 2B₂O₃→AlB₂ + Al₂O₃ and Al + TiO₂→Al₂O₃ + Al₃Ti. Therefore, it is quite acceptable that a similar chemical reaction from AlB₂+Al₃Ti to 4Al-TiB₂ must occur after when AlB₂ and Al₃Ti are formed in the Al-B-O-Ti quaternary system.

In order to form Al-TiB₂ 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 AlB₂ + Al₃Ti→4Al + TiB₂ was expected to be progressed during holding at 1000°C for 60min. During heating, two key reactions of Al+3Ti→Al₃Ti and Al+2B→AlB₂ 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 TiB₂ two phases. Figure 7 shows a SEM micrograph of Al-Ti-B after the heat treatment similar to Fig.5. The cuboidal particles were TiB₂ with the diameter being less than 1μm. besides, the composite was dense.
with matrix Al and precipitates TiB₂.

Therefore, it is concluded that the formation of AlB₂ and Al₃Ti and the reaction of AlB₂ + Al₃Ti → 4Al + TiB₂ are important rate controlling factors for the synthesis of Al-TiB₂ in-situ composites.

Conclusions

1. The reaction temperature of Ti + 2B → TiB₂ 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 → AlB₂ was recognized at about 700°C. The AlB₂ was decomposed at about 1050°C due to the peritectic reaction of AlB₂→(Al)+AlB₁₂.
3. The phase reaction of 3Al + Ti → Al₃Ti is easily taken place just after melting of Al.
4. The key reaction to form Al-TiB₂ in-situ MMCs is AlB₂ + Al₃Ti → 4Al + TiB₂, and this reaction was activated at about 900°C. Based on the chemical reactions, the maximum fraction of TiB₂ is evaluated to be 27.9vol%.
5. Both the two reactions of 3Al + B₂O₃ → Al₂O₃ + AlB₂ and 13Al + 3TiO₂ → 2Al₂O₃ + 6Al₃Ti were progressed at about 800°C.

Acknowledgements

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References

[19] Al-B phase diagram