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Formation of TiB_w reinforcement in *in-situ* titanium matrix composites

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Titanium matrix composites (TMCs) are being used widely in aerospace industries because of their excellent mechanical properties at room temperature and elevated temperature [1–5]. But their mechanical properties vary with the species and shape as well as size of reinforcement. Traditionally, TMCs are prepared by powder technology [6, 7] or liquid metallurgy [8], where ceramic particles are directly incorporated into solid or liquid matrixes. In recent years, TMCs are fabricated by *in-situ* techniques [9–11], where reinforcements form through liquid reactions. TMCs fabricated by *in-situ* techniques have better properties because they overcome the shortcomings of traditional techniques. Reactive sintering [12, 13] is one of *in-situ* techniques fabricating titanium matrix composites. In this process, exothermic reactions between powders facilitate *in-situ* formation of reinforcements. Advantages of reactive sintering of composites are able to obtain small-sized reinforcements over a wide range of volume fractions, together with clean and thermodynamic stable reinforcement-matrix interfaces. Ceramic particles, such as carbide, boride and nitride are used to reinforcements of titanium matrix composites. TiB is particularly suitable for as reinforcing phases in Ti-based reactive sintered composites because of its high exothermicity of formation and thermodynamic stability in Ti.

Although there have been much efforts [14–16] directed now to the study on *in-situ* formation of reinforcements in titanium matrix composites, there still is a lack of understanding of reaction mechanism, which hinders the optimization of Ti-TiB composite fabrication, including controlling the composition and the microstructure. Therefore the study on the formation of reinforcement is essentially for the attainment of excellent mechanical properties of composites. It is found [17] that *in-situ* synthesized TiB whiskers by adding of Al content into Ti-B become finer than pure Ti-B. Subsequently, the microstructure evolution [18] during *in-situ* forming TiB whiskers reinforced Ti matrix composite is studied. But the formation mechanism of TiB whiskers in Ti-B-Al system has not been clearly understood. In the present paper, the reinforcement's formation mechanisms and their phase formation sequence of the reactive sintering of Ti-TiB composites from elemental powders are studied. DTA is used to investigate thermal effects of the process and a combination of DTA and XRD is used to investigate the formation of *in-situ* TiB phase.

The material used in the present investigation is the mixture of Ti, B, and Al powders, and its composition is Ti-45 vol%TiB, which corresponds to a mixture of 88.3 m%Ti, 7.5 m%B, and 4.2 m%Al. These powders were blended and compressed into pellets. Samples were taken from the interior of the pellets. In the DTA experiments, samples were heated up to 1500 °C at a linear heating rate of 10 °C/min in a protective argon atmosphere.

The *in-situ* TiB phase formation sequence was investigated with XRD analysis of intermediate reaction products. The intermediate stages in the reactive sintering process were identified in the DTA experiments. Samples for XRD analysis of the intermediate stages in the reactive process were prepared in the DSC equipment, so as to ensure that the reaction was halted at the desired stage. Then samples were polished and etched, the microstructures corresponding to intermediate stages were observed with SEM.

The DTA curve for Ti-B-Al system is shown in Fig. 1. It can be seen clearly that multiple reactions happen while this system is being heated. These reactions include one endothermic reaction and two exothermic reactions. These reactions are indicated by "A", "B" and "C" in Fig. 1, respectively.

In Fig. 1, the temperature corresponding to the endothermic reaction, indicated by "B", is about 665 °C, which is almost melting point of Al. Before Al is melted, there is a small exothermic reaction, marked with "A", which is attributed to solid-solid surface diffusion reaction between Al and Ti powders. After Al is melted, the temperature corresponding to another exothermic reaction, "C" is 710 °C. It closely follows melting point. From the shape of reaction peak in DTA curve, it is known that this reaction releases a great deal of heat. Considering possible reactions in Ti-B-Al, it is considered as TiB formation, because free enthalpy (ΔH) of the reaction between Ti and B is up to 231–252 kJ/mol [19].

The next step in the investigation is to find out the influence of intermediate reactions on TiB formation and the reaction sequence in the Ti-B-Al system. On the basis of the DTA results of Fig. 1, samples were taken at intermediate stages of the reactive sintering process, that is, at 560 °C, reaction "A"; at 680 °C, after "B"; at 710 °C, reaction "C"; 750 °C, after "C"; and at 1500 °C. They are marked with "◆" in Fig. 1. Fig. 2a–e show the corresponding XRD patterns.

It is seen from Fig. 2a that there exists $TiAl_3$, TiAl and Ti phases at 560 °C, this temperature is lower than the melting point of Al, so Ti, B and Al powders are in pure solid state. At this temperature, the solid solubility

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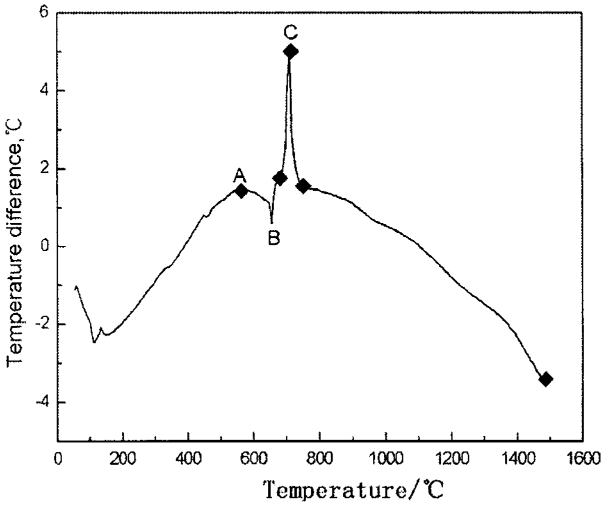


Figure 1 DTA curve of Ti-B-Al system.

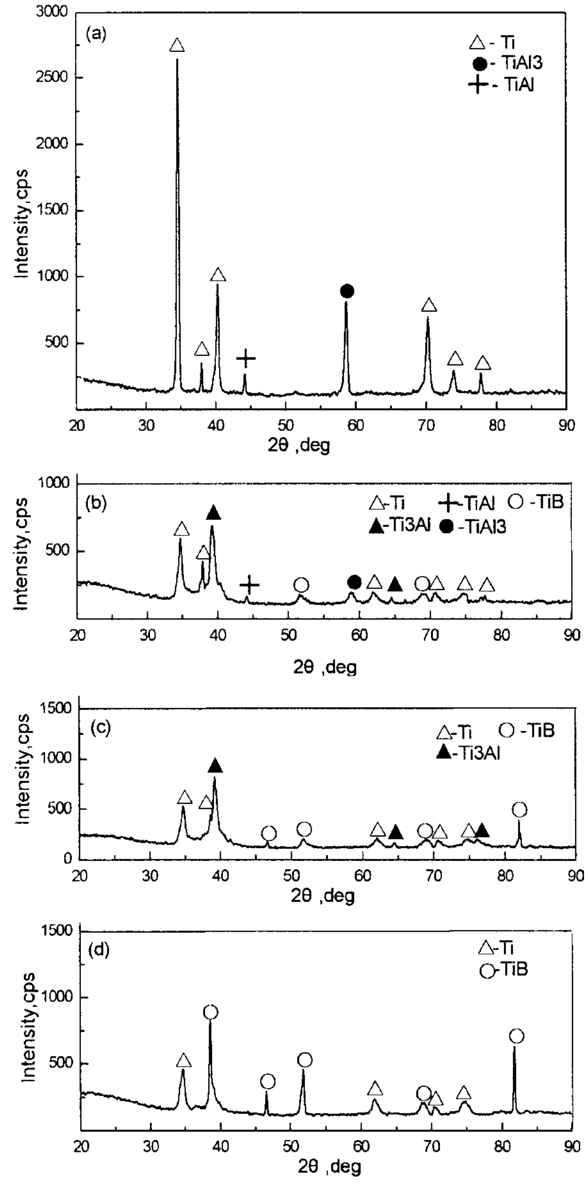


Figure 2 XRD patterns of samples quenched at: (a) 560 °C, (b) 680 °C, (c) 710 °C, and (d) 750 °C.

between Al and B is very low, as well as, solid solubility of B in Ti is less than 1 at.% when temperature is lower than 1540 °C [20]. Therefore, there is no boride formed. The $TiAl_3$, TiAl are products from solid-solid diffusion reactions between titanium and aluminum. Because their formation reactions in complete solid state are not intense, the reaction "A" shows a gentle exothermic peak in DTA curve.

At 680 °C, there are TiB, Ti_3Al phases, in addition to already existed $TiAl_3$, TiAl. But the amount of $TiAl_3$, TiAl decreases relatively compared with 560 °C. At this temperature, Al has been melted. Thus the reactions between titanium and aluminum are promoted. The reactions between titanium and aluminum are written as: $3Al + Ti \rightarrow TiAl_3$, $TiAl_3 + 2Ti \rightarrow 3TiAl$, $TiAl + 2Ti \rightarrow Ti_3Al$. These reactions release more heat and are accelerated in return. As a result, the amount of $TiAl_3$, TiAl decreases, while, the amount of Ti_3Al increases. The formation of TiB can be interpreted as follow: before Al is melted, it is difficult for Ti and B diffuse to each other without liquid phase. So, even there exists reaction heat from solid-solid diffusion between titanium and aluminum, the reactions to form TiB phases cannot initiate. Yet after Al is melted, liquid Al not only promotes titanium-aluminum reactions and a great lot of reaction heat release, but also accelerates interdiffusion between Ti and B. the double effects of liquid Al enable the reaction between Ti and B. The overall reaction sequence can be written as:

$$x\mathrm{Ti}_{(s)} + y\mathrm{Al}_{(l)} = \mathrm{Ti}_x\mathrm{Al}_{y(s)}$$

$$(x = 1, y = 1, 3;\ x = 3, y = 1) \quad (1)$$

$$\mathrm{Ti}_x\mathrm{Al}_{y(s)} + \mathrm{B}_{(s)} = \mathrm{TiB}_{(s)} + \mathrm{Al}_{(l)} \quad (2)$$

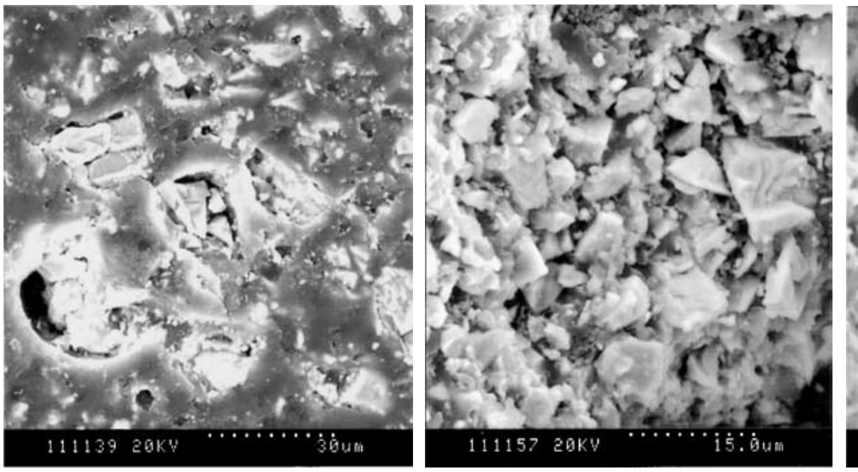
$$\mathrm{Ti}_{(s)} + \mathrm{B}_{(s)} = \mathrm{TiB}_{(s)} \quad (3)$$

At 710 °C , TiAl and $TiAl_3$ phases disappear and the amount of TiB, Ti_3Al increases compared with 680 °C. Because reactions to form TiB are exothermic, with increasing amount of TiB phases, a great deal of heat releases fast, thus TiB formation is expressed as a sharp exothermic peak "C" in Fig. 1.

At 750 °C , Ti_3Al disappears, there are only TiB and Ti phases in sample, and the amount of TiB increases further compared with 710 °C. It indicates that all reactions in Ti-B-Al system end, TiB phases were synthesized as unique reinforcement in Ti matrix.

While phases in intermediate stages are identified with XRD, it is noted that there is no Al detected. This is because that Al content is below the solid solubility limit for Al in Ti.

Moreover, Fig. 3a–c show microstructures formed at intermediate stages. In Fig. 3a, there are blocky phases, and some posse sharp tip pointed by an arrow. According to XRD results in Fig. 2a, these blocky phases are titanium-aluminum intermetallic compounds. Because packed together, they cannot be distinguished from each other. In Fig. 3b, the blocky phases are found in the whole sample. It is because that liquid Al accelerates reaction between titanium and aluminum, and the amount of titanium-aluminum intermetallic compounds increases, accordingly. Although TiB phases are detected in XRD results in Fig. 2b, there is no whisker seen due to little amount and fine size, Fig. 3c shows the microstructures at 710 °C. According to XRD results in Fig. 2c, the amount of TiB phase



(a) (b) (c)

Figure 3 Microstructures at intermediate stages: (a) 560 °C, (b) 680 °C, and (c) 710 °C.

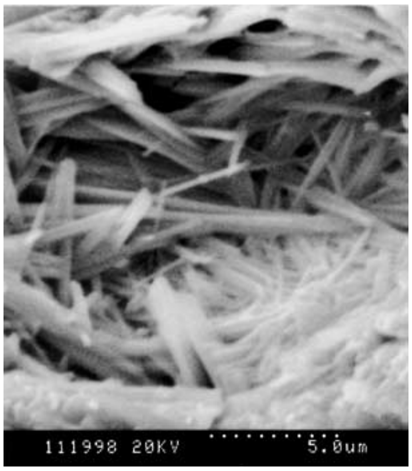


Figure 4 Microstructures of sample at DTA experimental temperature of 1500 °C.

increases compared with 680 °C. Therefore, TiB phases are clearly seen.

Fig. 4 shows morphology of TiB whiskers in sample at DTA experimental temperature of 1500 °C. In Fig. 4, it is seen that the TiB phases appear in whiskers. And the slender TiB whiskers are interlaced.

From discussions above, the formation mechanism of TiB in Ti-B-Al can be interpreted as following: before Al is melted, solid-solid diffusion reactions between titanium and aluminum happen and release heat. But it is not enough for initiating reaction between Ti and B to form TiB phase. With increasing temperature, Al is melted. Liquid Al promotes reactions between titanium and aluminum. Accordingly, the heat released from these reactions increases as well. This heat can be provided as the energy need by TiB formation. And, liquid Al serves as solvent, Ti and B diffuse each other at a relatively higher rate. Under the double effect brought by liquid Al, TiB phases form.

During TiB formation, $TiAl_3$, TiAl and Ti_3Al only exist as intermediate phases. They are in blocky shape. With increasing amount of TiB, they are decomposited successively. When all reactions end in Ti-B-Al system, TiB whiskers serve as unique reinforcement in Ti matrix.

Acknowledgments

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