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Microstructure and mechanical properties of TiBw/Ti-Ti_3Al metal-intermetallic laminate (MIL) composites

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Abstract. TiBw/Ti-Ti_3Al laminated composites have been fabricated through reaction annealing in vacuum using 5vol. % TiBw/Ti composite foils and Al foils with different initial thicknesses. The aluminum layer is consumed by forming a titanium aluminide intermetallic compound. Thus, the final microstructure consists of alternating layers of intermetallic compound and unreacted TiBw/Ti composite. Microstructural characterization by scanning electron microscopy (SEM), X-ray diffraction (XRD) has shown that only the intermetallic Ti3Al is formed. The designing laminated composites exhibit a superior combination of tensile strength and ductility during the tensile process.

1. Introduction

High temperature structural alloys have attracted more and more attention in structural applications [1, 2]. Ti-Al based intermetallic compound has become the most potential for high temperature structural materials due to the high melting point, high strength, high temperature creep properties and excellent resistance to high temperature corrosion [3-7]. However, the ductility at room temperature is extremely poor, which limits its use as a structural component [8-10]. To solve this problem, ensuring the strength properties of materials while improving its toughness through designing the microscopic structure has become the focus of current research. In recent years, people get inspired to design a "laminated composites" from the special structure of the shell with brittle layer and the organic composition of overlapping interactive, which has a high strength and toughness. This bionic design is based on the energy dissipation principle. The structural design thinking is to minimize the impact of raw crack defects on the mechanical properties of the material [11, 12]. Based on this idea, people found that intermetallic compound micro-laminate structure exhibited good toughness. For example, $TiAl_3$/Ti laminated composite synthesized in the previous work owning a higher specific strength and specific modulus compared with other metallic material [13]. Therefore, take advantage of the laminated structure, intermetallic compound/metal laminated composites prepared by intermetallic compound and toughness of metal phase enables materials having an energy dissipation structure of the stress field, overcome the intermetallic compound material due to poor toughness and the occurrence of unexpected rupture of the Achilles' heel. It has broad application prospect in the future [14-16].

Nowadays, Metal-intermetallic laminate (MIL) composites with laminate structures are designed to optimize the desirable mechanical properties of intermetallic by incorporating layers of ductile reinforcement, but the study on controlling process of Ti-Al system MIL with low density and high performance is still insufficient. In this study, TiBw/Ti-Ti_3Al laminated composites were prepared by using Al foils and TiBw/Ti composite foils as raw materials, stacking, and reaction annealing. The phase composition, microstructure and mechanical properties of the composites were investigated. These are beneficial to understand the relationships between structure and performance of the laminated composites, and then guide the subsequent microstructure design for other composite systems.

2. Experimental Procedures

Commercial pure Al foils and 5 vol. % TiBw/Ti composite foils based on the system of TiB_2/Ti powder mixtures were cut into 30×50 mm^2 squares, and then etched in 10 vol. % NaOH and 10 vol. % HF solutions to a final thickness of 100μm and 600μm, respectively. Alternating foils of TiBw/Ti (6 pieces) and Al (5 pieces) were stacked into a graphite mold. The laminates were subsequently subjected to hot pressing in vacuum (~10^{-2}Pa) under a pressure of 25MPa at 515 °C for 1.5h. Then, multi-step annealing was utilized to produce the desirable TiBw/Ti-Ti_3Al laminated composites. The multi-step annealing processes are specified in Table.1, and the corresponding purposes are given as follows: (a) the initial reaction annealing was subsequently performed in vacuum hot pressing sintering furnace (~10^{-2}Pa) at 680 °C for 1.5h to convert the entire elemental Al into $TiAl_3$, and the above process for the low temperature heat treatment stage, which can be described by the following reaction:

$$Ti+3Al \rightarrow TiAl_3 \quad (1)$$

Table 1. Annealing processes of multi-layered (TiBw/Ti)-Al composites.

Annealing processes	Temperature(°C)	Holding time (h)	Pressure (MPa)
Initial reaction annealing	680	1.5	0
Secondary reaction annealing	1150	6	20

(b) the secondary reaction annealing at 1150 °C for 6h under 20MPa was employed to obtain the desirable TiBw/Ti-Ti_3Al laminated composites, and the above process for the high temperature heat treatment stage, which can be described according to the following reaction:

$$TiAl_3+Ti \rightarrow Ti_3Al \quad (2)$$

Micro structural examination was performed by scanning electron microscopy (SEM, Hitachi S-4700) for the samples after etching by 5%HF+15%HNO_3+80%H_2O solution. Phase analysis of TiBw/Ti-Ti_3Al laminated composites was carried out by X-ray diffraction (XRD).

The density measurements were carried out using the buoyancy method with a TG328A (G) precision electronic balance with under-hook weighing.

The general tensile tests and the fracture toughness measurements were performed at room temperature using an Instron-1186 universal testing machine with a strain rate of $1 \times 10^{-4}\,s^{-1}$.Tensile dog bone samples have dimensions of 18×5×2mm^3 and the surfaces of the bone-like tensile specimens were carefully polished. The size of fracture toughness specimens was 4×2×20 $mm^3$with the span length of 16 mm and they were cut in parallel and perpendicular to the layered structure direction, respectively. The sample surfaces were mechanically polished and the straight notch was subsequentlyintroducedatthecenterpartofthetestbarusinga100μmwidediamondbladewithanotchdepthof0.5W(thewidthofthespecimen).

The computational formula of fracture toughness(K_{IC}, MPa·$m^{1/2}$)is:

$$K_{1C} = \frac{3PL\sqrt{10a}}{200bh^2}\left[1.93 - 3.07\left(\frac{a}{h}\right) + 14.53\left(\frac{a}{h}\right)^2 - 25.07\left(\frac{a}{h}\right)^3 + 25.80\left(\frac{a}{h}\right)^4\right]$$

Where P(N)is the maximum load when the specimens break, L(mm)is the span length, b(mm) is the width of specimen, h(mm) is the thickness of specimen and a(mm) is the length of the slit notch.

3. Results and Discussions

3.1 Microstructure Evolution during Annealing

Fig. 1a shows the microstructure of the hot-pressed (TiBw/Ti)-Al laminates. It can be seen from the cross section of the laminates that the interfaces between TiBw/Ti composite layers and pure Al layers were rather compact and no intermetallic compounds formed. Subsequently, the well-bonded (TiBw/Ti)-Al laminates were subjected to reaction annealing at 680 °C for 1 h without pressure to convert part of the elemental Al into $TiAl_3$, and thus the self-propagating low temperature synthesis (SLS) reaction between liquid Al and solid Ti occurred. After annealing at 680 °C for 1 h, the resulting microstructure consists of three phases, namely, TiBw/Ti (gray white region), the reaction $TiAl_3$ intermetallic compound (dark gray region) and the excess Al (dark region) as shown in Fig. 1b. Fig. 1c and Fig. 2b shows the structure and composition of the laminates after annealing at 680 °C for 1.5 h, it can be determined that Al foils were completely consumed, gray white layers and dark gray layers represented the TiBw/Ti layers and $TiAl_3$ layers, respectively. In $TiAl_3$ layers, numerous pores were formed. TiB whiskers did not participate in any reaction and showed a non-uniform distribution within TiBw/Ti layers. Then, the densification treatment was carried out under 20MPa at 1150 °C for 4h in vacuum heat treatment furnace. Fig. 1d and Fig. 2c show the structure and composition of the laminates. We can see that the $TiAl_3$ phase was disappeared and the Ti_3Al phase, the TiAl phase and the $TiAl_2$ phase were found. Finally, the time was raised to 6h under 20MPa. As shown in Fig. 1e, the pores were completely closed and the structure became uniform. Comparing with Fig. 2d, the TiAl phase and the $TiAl_2$ phase were disappeared, and the Ti_3Al phase was the only generation phase.

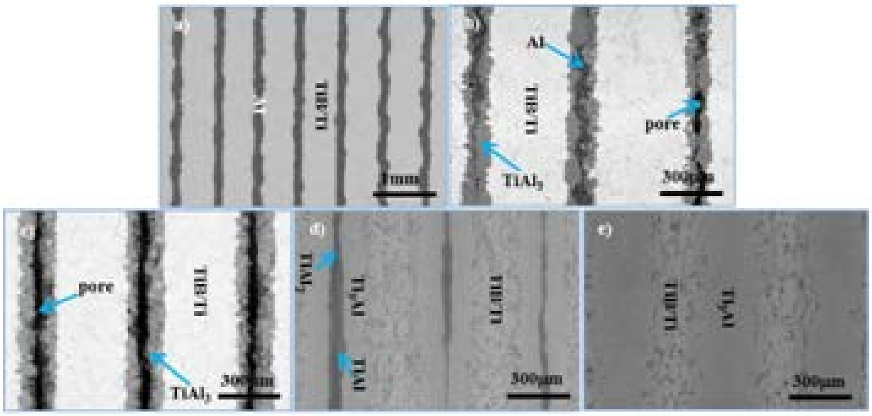

Figure 1. SEM image of microstructure of (TiBw/Ti)-Al laminates during annealing. (a) 515 °C for 1.5h under 25MPa; (b) 680 °C for 1h; (c) 680 °C for 1.5h;(d) 1150 °C for 4h under 20MPa; (e) 1150 °C for 6h under 20MPa.

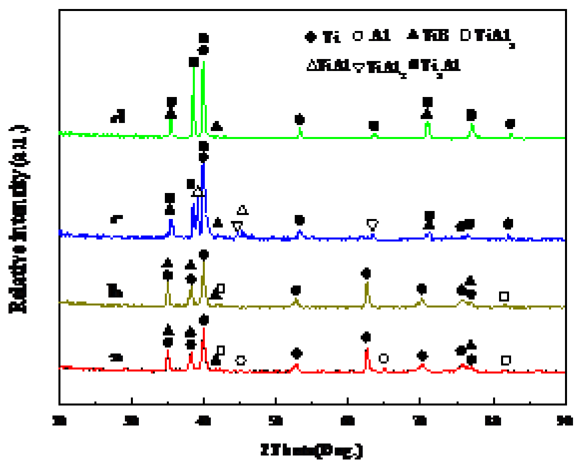

Figure 2. The phase composition of (TiBw/Ti)-Al laminates during annealing. (a) 680 °Cfor 1h; (b) 680 °C for 1.5h; (c)1150 °C for 4h under 20MPa; (d)1150 °C for 6hunder 20MPa.

3.2 Microstructure Characterization

The SEM micrographs of TiBw/Ti-Ti_3Al laminated composites are shown in Fig. 3a, which shows the thickness and the interface zone between the two layers of the TiBw/Ti-Ti_3Al laminated composites. The image displays that the two different layers are about 300μm and the interface zone between the two layers is clear and nearly straight. We can see from the cross section of the laminated composites that uniform layered structure without porosity and crack has formed, and the TiB whiskers is tightly fixed to the Ti particles and no micro-defects appeared due to clean reaction interface between Ti and TiB whisker, which indicates that a well-bonded composite structure can be achieved by the annealing process. The micrographs of TiBw/Ti-Ti_3Al laminated composites (OM) are shown in Fig. 3b, which displays the grain characteristics of two different layers. Relatively coarse grain size of Ti_3Al in the Ti_3Al layers, while relatively fine grain size of Ti matrix in the TiBw/Ti layers. In the Ti_3Al layer, it is to be found that many relatively fine equiaxed grains appear in the immediate zone of TiB whiskers but relatively coarse lath-like grains formed further away from TiB whiskers. It is because that equiaxed grains appear to nucleate and grow from TiB whiskers on slow cooling from high temperature annealing whereas lath-like grains usually form in those regions which do not contain TiB whiskers [24]. However, in the TiBw/Ti layer, there are many equiaxed grains in the absence of TiB whisker. Huang concluded that the equiaxed grains are due to isotropic tensile stress generated by phase transition from β(Ti) phase to α(Ti) phase on slow cooling during annealing process [25].Overall, TiB whiskers change the grain characteristic from lath-like grains into equiaxed grains at the interface. Meanwhile, the existence of TiBw/Ti composite layer restricts growth of Widmanstätten lath-like grains. Therefore TiB whiskers play an important role in changing the morphology and size of grains.

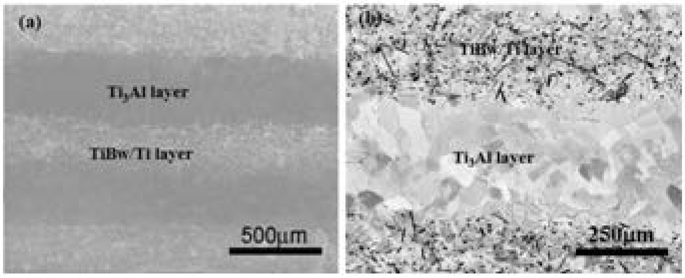

Figure 3.The micrographs of TiBw/Ti-Ti_3Al laminated composites. (a) SEMmicrographs and (b)OM micrographs.

3.3 Room Temperature Tensile Properties

The TiBw/Ti-Ti_3Al laminated composite exhibits a good combination of low density (4.36 g/cm^3), high yield strength (527 MPa) and ultimate strength (641 MPa) at room temperature (Fig. 4a), and its fracture morphologies are shown in Figs. 4b-d.As shown in Fig. 4b, river-like patterns were observed, which is similar to the previous literatures [19-22]. The fracture morphologies also indicated the typical transgranular-cleavage fracture mode in Ti_3Al layers. In addition, the crack preferred to propagate within Ti_3Al phases because the stress concentration at grain boundaries was not relieved and thus transgranular-cleavage fracture was the major failure mode.Compared to brittle fracture characteristics in the Ti_3Al layer, the TiBw/Ti composite layer reveals quasi-cleavage fracture morphologies, which is ductile fracture including regions of many dimples, micro-void coalescence, and flat “featureless” regions (Fig. 4c). It is found that many dimples appear at TiB whiskers lean zone, while micro-void coalescence emerge at the TiB whiskers rich zone, which indicates that the continuous matrix among the needle TiB whiskers can effectively play a toughening role. Furthermore, the breakage and pullout of TiB whiskers were found as shown in (Fig. 4c). This implied that TiB whiskers could increase the resistance to crack propagation, resulting in an enhancement of fracture toughness.Fig. 4c shows the interfaces between the Ti_3Al layer and the TiBw/Ti composite layer, it can be clearly seen from the fractograph that the interfaces are very rough, indicating tortuous crack propagation paths. There is no evidence of large Ti_3Al matrix rupture on the fracture surface and cracks always propagate along TiB whiskers (Fig. 4d), which reveals that the Ti_3Al matrix plays an effective role in bearing strain and obstructing crack propagation while TiB whiskers can bear stress and play an important role in strengthening composites during the tensile deformation. The room temperature mechanical performance of the TiBw/Ti-Ti_3Al laminated composites and monolithic Ti_3Al are shown in table2 and Fig. 4a. Especially, Fig. 4a compared the tensile strength and elongation histogram of the TiBw/Ti-Ti_3Al laminated composites and the monolithic Ti_3Al, respectively. The ultimate tensile strengths (σ_{UTS}) were 641MPa, 552MPa, respectively, the corresponding yield strengths (σ_y) were 527MPa, 550MPa, respectively, and the elongation were 8.7%, 0.3%, respectively. Compared to monolithic Ti_3Al, the ductility of the TiBw/Ti-Ti_3Al laminated composites is significantly improved. This means that the design strategy of laminated composites overcomes the inversion problem of strength and plasticity, achieving the expected design effect. The superior combination of tensile strength and ductility of the TiBw/Ti-Ti_3Al laminated composites attributed to the following reasons:

(1) The existence of TiB whiskers can restrict the growth of Ti_3Al matrix [17]; (2) The TiBw/Ti composite layer can delay the premature local necking of the Ti_3Al layer, which can effectively improve the elongation of Ti_3Al layer and (3) The multi-layered structure imparted extra deformation capacity by means of shielding or blocking generation of unstable cracks and thus had considerable contribution to the strength enhancement of the TiBw/Ti-Ti_3Al laminated composites [18].

In summary, compared to bulk materials, the multiple interfaces of laminated structure can effectively redistribute stress and inhibit strain localization by load-transferring to adjacent layers, which provide another way for stress-transferring, and this has been investigated in the previous work [23]. So, the crucial fracture modes not only based on the material of individual layer, but also may depend on the thickness ratio of the two individual layers. This is an interesting issue to be discussed in our later work.

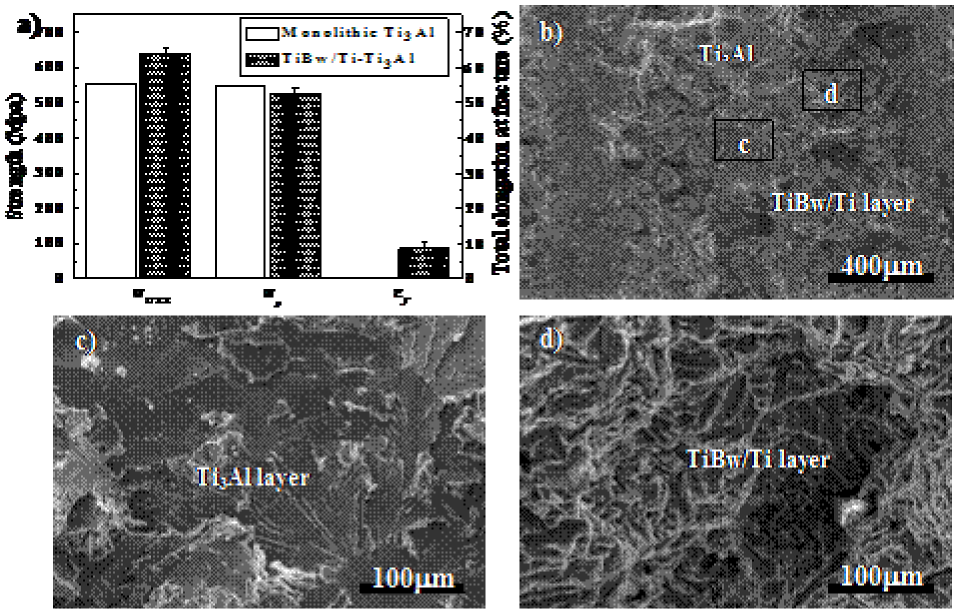

Figure 4. (a) Room temperature mechanical performance histogram of the monolithicTi_3Al and the TiBw/Ti-Ti_3Al laminated composites; (b)overall fracture surface of the TiBw/Ti-Ti_3Al laminated composites; (c) fracturesurfaceofTi_3Al layer; (d)fracture surface of TiBw/Ti composite layer.

3.4 Fracture Analysis

Table2 shows the fracture toughness histogram of the monolithic Ti_3Al and the TiBw/Ti-Ti_3Al laminated composites with different loading directions. It can be clearly seen that the fracture toughness of the TiBw/Ti-Ti_3Al laminated composites with the notch perpendicular to the layered structure direction (Arrester orientation) is 227% higher than the fracture toughness of the monolithic

Ti_3Al [23]. and the fracture toughness of the TiBw/Ti-Ti_3Al laminated composites with the notch parallel to the layered structure direction (Divider orientation) is 142% higher than the fracture toughness of the monolithic Ti_3Al. Fig. 5a-d illustrates the fracture surfaces of the TiBw/Ti-Ti_3Al laminated composites with different loading directions. As shown in Fig. 5a-b, ligament-bridge and crack deflection were found in the TiBw/Ti-Ti_3Al laminated composites, which facilitated the improvement of fracture toughness in comparison with the monolithic Ti_3Al. As shown in Fig. 5c-d. The fracture surfaces were quite flat exhibited the tragranular and cleavage fracture features for the TiBw/Ti-Ti_3Al laminated composites with different loading directions, respectively. In general, the Ti_3Al layers showed the brittle features. However, the facture surfaces were obviously much rougher and exhibited faceted fracture with some ductile dimples at TiBw/Ti layers. In particular, some cavities were formed during the parting process and tearing striations were present on the fracture surfaces of the TiBw/Ti-Ti_3Al laminated composites, which indicated that the laminated composites have undergone remarkable plastic deformation prior to final fracture. Again, the breakage and pullout of TiB whiskers were found, this implied that the addition of TiBw whisker has indeed contributed to a prominent enhancement in the ductility of the TiBw/Ti-Ti_3Al laminated composites. Furthermore, crack propagation path in the arrester orientation was more tortuous, in contrast to that in the divider orientation, resulting in the higher energy consumption, and thus the better fracture toughness was achieved. Additionally, the fracture toughness of the TiBw/Ti-Ti_3Al laminated composites was higher than the value of the laminated composites reported by the previous references [18, 26-27]. The reason was attributed to:

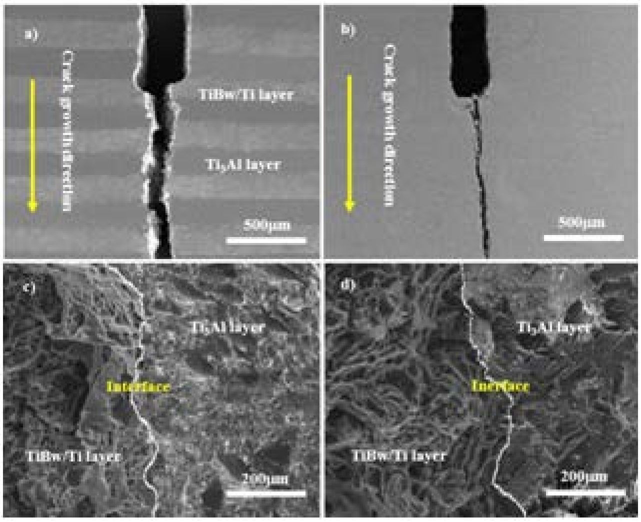

Figure 5. Crack propagation path morphology in the TiBw/Ti-Ti_3Al laminated composites in (a)perpendicular tothe layered structure direction (Arrester orientation) and (b) parallel to the layered structure direction (Divider orientation)and the correspondingfracture surfaces in (c)arrester orientation and(d) divider orientation.

Table 2. Room temperaturemechanical performance comparison between TiBw/Ti-Ti_3Al laminated composites and monolithicTi_3Al.

System	σ_{UTS} (MPa)	σ_y(MPa)	δ(%)	K_{IC}(MPa·m$^{1/2}$)	
				Arrester orientation	Divider orientation
TiBw/Ti-Ti_3Al	641±7	527±6	8.7±0.4	33.7±0.4	24.9±0.3
Monolithic Ti_3Al	552	550	0.3	10.3	

σ_{UTS}, σ_y and δ *of* monolithicTi_3Al[26]; K_{IC} *of* monolithicTi_3Al[23].

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(1) The multi-layered structure imparted extra deformation capacity by means of shielding or blocking generation of unstable cracks;(2) The addition of TiB whisker refines the grain size of the TiBw/Ti-Ti_3Al laminated composites and improves the fracture toughness of the composites and(3) TiB whisker with high aspect ratio consumes more energy in the process of crack deflection. Therefore, the following work will be focus on improving the fracture toughness of the TiBw/Ti-Ti_3Al laminated composites by controlling the volume and content of the TiB whiskers.

4. Conclusions

(1) TiBw/Ti-Ti_3Al laminated composites composed of alternating TiBw/Ti layers and Ti_3Al layers were successfully fabricated by reaction annealing. Compared to monolithic Ti_3Al, the TiBw/Ti-Ti_3Al laminated composites overcomes the inversion problem of strength and plasticity and exhibits a superior combination of tensile strength and ductility.

(2) The addition of TiBw/Ti layer significantly improves the elongation and fracture toughness of the TiBw/Ti-Ti_3Al laminated composites by means of shielding or blocking generation of unstable cracks. The TiB whisker refines the grain size of the TiBw/Ti-Ti_3Al laminated composites, consumes more energy in the process of crack deflection and plays an important role in strengthening composites during the tensile deformation.

(3) The TiBw/Ti-Ti_3Al laminated composites reveal different fracture mechanisms in TiBw/Ti layers and Ti_3Al layers. Ti_3Al layer reveals brittle fracture mechanism river-like patterns. However, TiBw/Ti composite layer exhibits ductile fracture mechanism with many voids and cracks initiated by fractured TiBw.

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