Strong and Ductile \textit{in Situ} Titanium Matrix Composites Reinforced by Titanium Boride Whiskers

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Abstract. A facile industrial processing route with low production costs was developed to produce \textit{in situ} TiB\textsubscript{w}/Ti matrix composites with a network reinforcement distribution. The formation mechanism, microstructure and mechanical properties are characterized. In contrast to traditional homogeneous TiB\textsubscript{w}/Ti counterparts with uniform reinforcement distribution, the present material exhibited a comparable ultimate strength, a good fracture toughness of 33.7 ± 0.3 MPa\textperiodcentered m\textsuperscript{1/2}, and a significantly elevated tensile ductility increasing by 58% at room temperature. Superior elongation to fracture as large as 67% at 700 °C demonstrated the potential for the follow-up thermo-mechanical processing or forming. Therefore our work may provide inspirations of fabricating cost-effective high-performance metallic structural materials through the tailoring of interfacial cohesion and reinforcement distribution.

1. Introduction

Strengthening metals via dispersed particles interacting with mobile dislocations invariably compromise the toughness and ductility [1, 2]. A great deal of research work have demonstrated the strength-ductility trade-off dilemma and easy failure by matrix/reinforcement interfacial decohesion of metal matrix composites [3-7]. Also, the strategy of tailoring the kind, morphology, amount, and spatial distribution of reinforcements, as well as the interfacial configuration, has been widely explored in the past few decades [8-10]. Dispersing the reinforcement as uniformly as possible is well acknowledged as one of effective methods to improve the mechanical properties of metal matrix composites [11]. As an important branch, titanium matrix composites with a homogeneous reinforcement distribution are generally synthesized by powder metallurgy (PM) technique, in which high-energy ball milling is required to ensure the sufficient mixing between the matrix and reinforcement, with deficiencies of the breaking of surface morphology and oxygen contamination [12]. Therefore PM-processed composites usually exhibited inferior mechanical performance in particular for tensile ductility against industrial applications.

The aim of this work is to develop a cost-effective processing route for the fabrication of high-performance metallic composites through microstructural design and constituent optimization. Commercially pure Ti was selected as the matrix for simplification and reinforced by needle-like TiB\textsubscript{w} with high aspect ratio and comparable thermal expansion coefficient. A low-energy ball milling followed by vacuum hot pressing was preformed to produce \textit{in situ} TiB\textsubscript{w}/Ti matrix composites with a network reinforcement distribution. The microstructure, formation mechanism, fracture toughness and tensile properties were characterized and evaluated in detail.
We first elaborated the design principle and fabrication processing of \textit{in situ} TiB$_w$/Ti matrix composites used in the present study. Commercial pure Ti and its alloys are known as one of the major workhorse materials for both industrial and structural applications, because they have good deformability that permits arbitrary shape change without cracking, and also provide clean matrix templates for delicate design of high-strength metallic materials through the addition of reinforced phases with morphologies of fiber, particle, or whisker [13]. Our recent work has demonstrated that the mechanical properties of metal matrix composites were mainly governed by the degree of microscopic strain localization, obeying the rule of “the greater the efficiency of strain transfer, the less the degree of plastic flow localization, the larger the deformation stability, and the better the performance” [11]. Such a mechanism is seemingly uncommon, and can be understood by the fact that the plastic instability of macroscopic necking is a result of incessant accumulations of microscopic strain localization at the necking region [1]. In this work, needle-like TiB whisker (TiB$_w$) with high aspect ratio was thus used as reinforcements to maximize the ability of strain transfer and to effectively strengthen Ti matrix. Additionally, the TiB$_w$ reinforcement possessed high elastic modulus and hardness, as well as comparable density and thermal expansion coefficient with those of Ti matrix, and the latter is of scientific importance to reduce the residual stress during thermomechanical processing [14].

2. Experimental Procedure

2.1. Sample Preparation and Microstructure Characterization

Commercially spherical Ti powders (99.9\% purity) with average particle sizes of 100 $\mu$m and prismatic TiB$_2$ powders with mean particle sizes of 4 $\mu$m were used as raw materials. Mixtures of Ti and TiB$_2$ were firstly ball milled in a planetary blender at a milling rate of 150 rpm for 6 h under an argon atmosphere. Hardened steel milling vessels and balls were utilized with a ball-to-powder weight ratio of 4:1. The blended powder mixtures were then placed into a specialized graphite mould and vacuum hot pressed at 1200 $^\circ$C for 40 min under a pressure of 20 MPa. The \textit{in situ} 5vol.% TiB$_w$/Ti matrix composites were thus fabricated through an \textit{in situ} reaction of Ti + TiB$_2$ $\rightarrow$ TiB$_w$.

The microstructures of as-sintered TiB$_w$/Ti matrix composites were examined by OLYPUS PMG-3 optical microscope (OM) and FEI Quanta 200F scanning electron microscope (SEM). Samples were mechanically ground, polished, and chemically etched using a Kroll solution of 5vol.% HF, 15vol.% HNO$_3$, and 80vol.% H$_2$O.

2.2. Mechanical Testing

The mechanical properties of as-sintered TiB$_w$/Ti matrix composites were evaluated by three-point bending and uniaxial tensile testing. Single-edge notched specimens with gauge dimensions of 16 mm in length, 2 mm in width, and 4 mm in thickness were employed to measure the fracture toughness. The notch depth was about 2 mm parallel to the loading direction. Three-point bending experiments were conducted on an Instron-5500 Universal Testing Machine with a crosshead rate of 0.5 mm/min. The extracting of maximum force, $F_{\text{max}}$, from automatically acquired load-displacement curves, gives the value of fracture toughness according to Eqs. (1) and (2):

$$K_{IC} = \frac{F_{\text{max}} S}{B^{1/2} W^{3/2}} \times f\left(\frac{a}{W}\right)$$

$$f\left(\frac{a}{W}\right) = 3\left(\frac{a}{W}\right) \frac{1.99 - \left(\frac{a}{W}\right)(1 - a/W)(2.15 - 3.93\left(\frac{a}{W}\right) + 2.70\left(\frac{a}{W}\right)^2)}{2(1 + 2a/W)(1 - a/W)^{3/2}}}$$

Here $B$, $S$, and $W$ are the thickness, span, and width of the specimen, respectively, with units of centimetre, $a$ is the length of a pre-crack, and $f(a/W)$ represents the geometry factor. According to the ASTM E1820 [15], we take $B=2$ mm, $S=16$ mm, $W=4$ mm, $a=2$ mm.

The dog-bone tensile plate specimens with gauge dimensions of 2.5 mm width by 15 mm length by 1.5 mm thickness were prepared by electrical discharge machining. Before tensile tests, the samples
were mechanically ground and polished using 0.5 μm diamond suspension. The uniaxial tensile tests were performed at room temperature (RT) and elevated temperatures (500~700 °C) using an Instron-1186 Universal Testing Machine at a constant strain rate of 1×10⁻³ s⁻¹. The tensile tests were repeated three times to obtain reproducible tensile properties.

3. Results and Discussion

3.1. In Situ Fabrication of TiBₓ/Ti Matrix Composites

Figure 1 shows the reaction synthesis, processing, and microstructure of in situ 5vol.% TiBₓ/Ti matrix composites. The TiBₓ reinforcement was found to be distributed, like the role of “grain boundary”, around the matrix particles with a grain size almost equal to that of as-received Ti powders. The formation of network distribution of TiBₓ was ascribed to the low-energy ball milling and solid-phase hot pressing sintering. More specifically, the application of low-energy milling did not significantly change the powder morphology and size, but uniformly attached the TiB₂ inclusions onto the surface of Ti matrix particles (Figures 1a and 1b). No voids or cracks were found in the as-sintered sample as shown in Figure 1c. Additionally, the solid-phase sintering restricted the reaction of Ti + TiB₂ → TiBₓ, only taking place at the surface not in the Ti grain interior (Figures 1d, 1e and 1f). Therefore a unique network structure was created and successfully produced in the present TiBₓ/Ti matrix composite through a simple powder metallurgy technique.

![Figure 1](image_url)

Figure 1. Reaction synthesis process of in situ 5vol.% TiBₓ/Ti matrix composites. (a) Low- and (b) high-magnification images of TiB₂ particle and Ti powders after low-energy ball milling. (c) Morphology, (d) X-ray diffraction, (e) low- and (f) high-magnification optical images of as-sintered 5vol.% TiBₓ/Ti matrix composites.

3.2. Mechanical Properties of TiBₓ/Ti Matrix Composites

Three-point bending testing was performed to measure in-plane fracture toughness at room temperature. Figure 2 shows a comparable value of 33.7 ± 0.3 MPa·m⁰⁵ of our in situ TiBₓ/Ti matrix composites relative to pure Ti. That is to say, the presence of 5vol.% TiBₓ did not significantly decrease the toughness of the composite. Careful examinations of fracture surface indicated many
interesting phenomena: (i) upon bending, needle-like TiB₆ with extreme brittleness was cracked but immediately blunted by the plastic flow of neighbouring Ti matrix (Figure 3). Therefore the initial cracking of TiB₆ may not contribute to the formation of critical major crack. (ii) Multiple cracking of TiB₆ was detected in Figure 3b, implying that the role of TiB₆ on stress transfer was always operating no matter it was intact or not; in other words, despite breaking, each TiB₆ segments can be reloaded by the ductile Ti matrix via the interfacial shear stress that the latter exerted [16], which disperses the externally imposed stresses and on the other hand prevent the severely unstable crack propagation behaviour. (iii) Plenty of secondary cracks, tortuous crack path, rough fracture surface, and reinforcement/matrix interfacial decohesion were clearly observed, which effectively consumed energy during the fracture process and imparted the toughness to the composite.

Figure 2. Room temperature fracture toughness of in situ 5vol.% TiB₆/Ti matrix composites. Experiments were repeated three times for representative statistics, giving a value of 33.7 ± 0.3 MPa·m¹/².

Figure 3. (a) Low- and (b) high-magnification secondary electron (SE) image of fracture surface of TiB₆/Ti matrix composites after three-point bending.

We next evaluated the mechanical properties of in situ 5vol.% TiB₆/Ti matrix composites with a network reinforcement distribution. At room temperature, the ultimate tensile strength was experimentally measured as 740 MPa, the same order of magnitude compared to homogeneous counterparts with the same constituents and uniform reinforcement distribution [14]. However, the ductility is much higher, up to 19% and increasing by 58% [14], highlighting the advantage of network reinforcement distribution. Such a dramatically enhanced elongation without compromising the tensile strength is due to the unique reinforcement distribution which changes the stress field both
microscopically and macroscopically and thus promotes the stress/strain transfer efficiency [17-20]. Elevating the temperature inevitably decreased the ultimate tensile strength down to about 220 MPa at 500 °C and 166 MPa at 600 °C as shown in Figure 4. At an ultrahigh condition of 700 °C exceeding the service tolerance accompanied by severe oxidation, our fabricated composites still sustained an ultimate strength of nearly 73 MPa, and hence provided inspirations for the design and development of advanced high-temperature Ti alloys through the tailoring of the reinforcement morphology and distribution.

Figure 5 shows the fracture topology of TiB₆/Ti matrix composites. All panels are in the same scale. The surface roughness, dimples, and tear ridgelines of the matrix were increasingly notable with increasing testing temperatures. Local micro-voids, corresponding to the pull-out of TiB₆, were also clearly observed, which revealed that the strengthening efficiency of TiB₆ reinforcements has been utilized sufficiently due to the strong interfacial cohesion between \textit{in situ} formed TiB₆ and Ti matrix. The plastic flow indicators of fine and deep dimples also suggested a good tensile elongation, e.g., as large as 67% at 700 °C (Figure 4).

**Figure 4.** True stress-strain curves of TiB₆/Ti matrix composites at high temperatures.

**Figure 5.** Fracture morphology of TiB₆/Ti matrix composites. The tensile testing temperatures were labelled on the left bottom corner of each panel.
4. Conclusions
A network distribution of TiB\textsubscript{w} in Ti matrix has been successfully produced by a low-energy ball milling followed by reaction hot pressing. The TiB\textsubscript{w} reinforcements were in situ synthesized around the boundaries of Ti matrix particles, forming a typical three-dimensional network structure. Compared to homogeneous counterparts with uniform reinforcement distribution, our TiB\textsubscript{w}/Ti composites showed a good ultimate strength, fracture toughness and a much higher tensile ductility, due to the enhanced stress transfer capacity of needle-like TiB\textsubscript{w} with a high aspect ratio. Such a strategy of tailoring the morphology and distribution of reinforcements may shed light on the design of next-generation high-performance metallic structural materials.

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