Effect of aspect ratios of in situ formed TiB whiskers on the mechanical properties of TiB\textsubscript{w}/Ti–6Al–4V composites

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Titanium alloys have been noted as promising high-strength structural materials for aerospace, military and automotive applications owing to their superior physical and chemical properties, such as high specific strength and corrosion resistance [1–4]. Despite the desirable properties of Ti alloys, their applications are often limited due to their relatively low specific stiffness and wear resistance. To obtain an enhanced elastic modulus as well as improved hardness to wear in Ti alloys, researchers over the years have developed a variety of Ti-based materials using ceramic reinforcements or by changing the alloying agents [5–9]. Among the materials developed, Ti alloys matrix composites (TMCs) reinforced using disparate ceramics as reinforcing agents have been of great interest because they allow performance tailoring, which results in high mechanical properties as well as superior wear resistance [5,10,11].

A number of reported TMCs reinforced by Ti\textsubscript{5}Si\textsubscript{3}, CrB, B\textsubscript{4}C, SiC [12] and TiC [13] show highly acceptable mechanical properties, but severe degradation can be induced by the large differences in the coefficients of thermal expansion (CTEs) between these ceramic reinforcements and a Ti matrix. Thus, several researchers [5,10–12,14–17] have reported Ti alloys reinforced by in situ formed Ti boride whiskers (TiB\textsubscript{w}), which have a CTE similar to that of the Ti matrix and good chemical stability. However, it is unfortunately difficult to fabricate TiB\textsubscript{w} with an aspect ratio of more than 10 in TMCs when conventional powder sintering processes requiring a long sintering time are used, as the growth of TiB\textsubscript{w} can occur isotropically within a short time. Furthermore, although there are many reports of mechanical properties, such as the yield strength and elastic modulus, being enhanced by TiB whiskers in TMCs, the origin of this type of strengthening has so far remained unclear.

In this study, we report a Ti–6Al–4V alloy reinforced by TiB\textsubscript{w} with a high aspect ratio of 58. The TMCs were fabricated by a spark plasma sintering (SPS) process, which is highly useful when seeking to control the anisotropic growth of TiB\textsubscript{w} with initially size-controlled TiB\textsubscript{2} powders. TMCs having various aspect ratios of TiB\textsubscript{w} were then prepared, and their microstructures and
mechanical properties were investigated in an effort to clarify the effect of the aspect ratio of TiB\textsubscript{w} on the mechanical properties of the TMCs. In particular, TMCs reinforced by relatively thin TiB\textsubscript{w} with a diameter of approximately 100 nm, resulting in an aspect ratio of 58, shows a strengthening efficiency that is three times that of TMCs with TiB\textsubscript{w} with an aspect ratio of 10.

TiB\textsubscript{2} (99%, 3 μm, KOJUNDO) and Ti–6Al–4V (99%, 43 μm, Koralco Corporation) powders were used in this investigation. The TiB\textsubscript{2} powders were milled to average sizes of 500 nm and 1 μm using a high-energy ball milling machine (Planetary Mill, Fritsch GmbH). The sizes of the TiB\textsubscript{2} particles were initially controlled by using a planetary milling process for specific milling times to obtain TiB\textsubscript{w} with various diameters. Three differently sized TiB\textsubscript{2} powders were mixed with Ti–6Al–4V powders via a high-energy ball milling process for 18 h at 250 rpm under an argon atmosphere. The mixed TiB\textsubscript{2}/Ti–6Al–4V powders were sintered into button-type bulk samples using an SPS system (Dr. Sinter Lab., Sumitomo) at 1200 °C for 5 min in a vacuum (10\textsuperscript{-3} torr) at a pressure of 50 MPa. A scanning electron microscope (SEM; HITACHI-S4800) and a transmission electron microscope (TEM; Tecnai G2 F39 S-Twin) were used for the observation of the microstructure in the TiB\textsubscript{w}/Ti–6Al–4V composite. The tensile properties of the TiB\textsubscript{w}/Ti–6Al–4V composite were determined using an INSTRON 4206 device at a crosshead speed of 0.2 mm min\textsuperscript{-1}.

To synthesize Ti alloys reinforced by TiB\textsubscript{w}, TiB\textsubscript{2} and Ti–6Al–4V powders were mixed. As shown in Figure 1(a), which shows the surface morphology of the mixed powders, the TiB\textsubscript{2} powders were homogeneously dispersed and embedded in a Ti matrix. The TiB\textsubscript{2} powders as displayed in the schematic illustration of Figure 1(a) were transformed in situ into TiB whiskers in the Ti matrix via an SPS process. Previous researchers [10,17–20] reported that, since the growing velocity of the longitudinal direction is much faster than that of the transverse direction but TiB has its own crystal structure, the shape of the in situ formed TiB is changed into a whisker with a hexagonal transverse section [20]. Similarly, boron atoms in the TiB\textsubscript{2} were diffused more rapidly and hence grew in the longitudinal direction rather than the transverse direction of the TiB whisker. They were stacked in the longitudinal direction of TiB\textsubscript{w} and then stacked in the transverse direction while maintaining the length of the TiB\textsubscript{w}. That is, the diameter of the TiB\textsubscript{w} decreases as the TiB\textsubscript{2} particle size decreases, leading to a high aspect ratio. Thus, we attempted to use size-reduced initial TiB\textsubscript{2} particles in an effort to obtain high-aspect-ratio TiB whiskers and adopted the SPS process to control the rapid growth of the TiB\textsubscript{w}.

We controlled the diameter and aspect ratio of the TiB\textsubscript{w} as a function of the TiB\textsubscript{2} particle size via a high-energy milling process, as shown in Table 1. As expected, the diameter of the TiB\textsubscript{w} increased as the TiB\textsubscript{2} particle size increased. As seen in Table 1, there were no significant differences in the grain sizes or the microstructure of the TiB\textsubscript{w}/Ti–6Al–4V matrix composites with different TiB\textsubscript{2} particle sizes. However, only part of the aspect ratio of the TiB\textsubscript{w} was increased markedly as the diameter of the TiB\textsubscript{w} in the TiB\textsubscript{w}/Ti–6Al–4V composite was decreased. Additionally, the aspect ratio was reduced upon the addition of more TiB\textsubscript{2} powder.

Figure 1(b) shows the surface morphology of 1 vol.% TiB\textsubscript{w}/Ti–6Al–4V composites, in which TiB whiskers of 100 nm diameter are networked three dimensionally in the matrix after the SPS process. The networked TiB whiskers were revealed by removing the Ti matrix from the composite by chemical etching. TEM image and selected area diffraction pattern of (c) a cross-section of TiB\textsubscript{w} in the plane of the diameter and (d) a cross-section of TiB\textsubscript{w} in the longitudinal direction, respectively.

Table 1. Aspect ratios of the TiB whiskers synthesized by varying the initial size of TiB\textsubscript{2} powders, grain sizes and relative densities of the TiB\textsubscript{w}/Ti–6Al–4V composite with various aspect ratios of TiB\textsubscript{w}.

<table>
<thead>
<tr>
<th>Initial TiB\textsubscript{2} powders</th>
<th>TiB\textsubscript{w}/Ti–6Al–4V composite</th>
<th>Grain size</th>
<th>Relative density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt.%</td>
<td>Size (μm)</td>
<td>Average diameter (μm)</td>
<td>Aspect ratio</td>
</tr>
<tr>
<td>0.5</td>
<td>500 nm</td>
<td>100 nm</td>
<td>58</td>
</tr>
<tr>
<td>1 μm</td>
<td>500 nm</td>
<td>500 nm</td>
<td>38</td>
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<tr>
<td>3 μm</td>
<td>1 μm</td>
<td>1 μm</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>3 μm</td>
<td>1 μm</td>
<td>13</td>
</tr>
</tbody>
</table>

Figure 1. (a) A surface SEM microstructure and a schematic illustration of TiB\textsubscript{w}/Ti–6Al–4V composite powders fabricated by a mechanical alloying process. (b) A field emission SEM surface morphology of 1 vol.% TiB\textsubscript{w}/Ti–6Al–4V composites with ~100 nm diameter of TiB\textsubscript{w}; the inset image shows the TiB whiskers with diameters of ~100 nm, ~500 nm and 1 μm, as revealed by removing the Ti matrix by chemical etching. TEM image and selected area diffraction pattern of (c) a cross-section of TiB\textsubscript{w} in the plane of the diameter and (d) a cross-section of TiB\textsubscript{w} in the longitudinal direction, respectively.
the surface by chemical etching. We confirmed the overall characteristics of the microstructures, including the grain size and the alpha/beta phases of the Ti matrix, as well as size and shape of the TiBw. There is only the difference in the diameter of TiB whiskers with ~100 nm, ~500 nm, and 1 μm as shown in the insets of Figure 1(b) and Table 1. Furthermore, the cross-sectional TEM images in Figure 1(c) and (d) confirm the growth direction of the TiBw and the phases of TiBw and Ti–6Al–4V, respectively. It was noted that the cross-section of the in situ TiBw is characterized by (100), (101) and (101) crystal planes with a hexagonal shape. In addition, the growth in the longitudinal direction of the TiBw is in the [010] direction, as reported in earlier studies [17–20].

It was reported that the diameter and length of the TiBw have quite different growth rates; TiBw generally grow at a higher growth rate in the longitudinal direction than in the transverse direction. In our case, the growth of TiB whiskers toward the diameter-direction was efficiently restricted by reducing the size of the TiB2 powders at the same amount. Even though the size of the TiB whiskers changed with the size of the TiB2 particles, we think that the inter-particle spacing between the TiB2 particles is not much different from the inter-particle spacing between the TiB2 particles in the microstructures. This is because the TiB whiskers are formed in random directions at the TiB2 particles and the length of the in situ formed TiB whiskers is about 5–10 μm, which is much larger than the TiB2 particle size. Therefore, it is expected that the aspect ratio of the TiB whiskers is a major factor in the strengthening effect, which acts through transferring load from the Ti–6Al–4V matrix to the whiskers in the TiBw/Ti–6Al–4V composite.

The elastic modulus (Ec) and the yield strength (σc) of a TiBw/Ti–6Al–4V composite with TiBw of different aspect ratios were measured by tensile testing. The measured values of both Ec and σc of the TiBw/Ti–6Al–4V composite exhibited enhanced behaviors upon increasing the aspect ratio of the TiB whiskers. As shown in Figure 2(a), the measured Ec value of the TiBw/Ti–6Al–4V composite is in good agreement with the value estimated assuming the use of the shear-lag model [21] based on the load-transfer concept between a matrix and randomly oriented reinforcements. At 1 vol.% of TiBw, the Ec value increases upon an increase in the S value from 18 to 58. The Ec value then increases from 116 to 125 GPa, following the line estimated at an aspect ratio of 10 as a function of the volume fraction. Hence, we can speculate that the stiffening mechanism in a TiBw/Ti–6Al–4V composite can be explained in terms of the load-transfer concept assuming that the interface is perfectly clean without the formation of any compound. We also calculated the σc value of the TiBw/Ti–6Al–4V composite using a generalized shear-lag model [22,23] because the shape of TiBw is assumed to be cylindrical. We calculated σc using the following equation:

\[ \sigma_c = V_f \sigma_m \frac{S}{2} + \sigma_m \]  

(1)

where \( V_f \) is the volume fraction of TiBw, \( S \) is the aspect ratio of the reinforcement (TiBw), \( \sigma_m \) is the yield strength of the matrix and \( \sigma_c \) is the yield strength of the composite. As shown in Figure 2(b), we plotted the estimated \( \sigma_c \) as a linear function of \( V_f \) using Eq. (1) when \( V_f \) ranges from 1 to 5 and \( S \) ranges from 10 to 60. The measured \( \sigma_c \) value of TiBw/Ti–6Al–4V composites reinforced by TiBw with different aspect ratios is in good agreement with the lines calculated while varying the \( S \) factor. This result also corroborates the contention that an efficient load transfer from Ti–6Al–4V to TiBw enables the strengthening of a TiBw/Ti–6Al–4V composite. The strengthening efficiency of the TiBw/Ti–6Al–4V composite can be expressed by the following equation:

\[ \sigma_c = \sigma_m (1 + V_f R) \]  

(2)

In this equation, \( R \) is the strengthening efficiency of the reinforcement, \( V_f \) is the volume fraction of the reinforcement (TiBw) and \( \sigma_m \) is the yield strength of the matrix. The \( R \) value is defined as the ratio of the increase in yield strength of the composite to that of the matrix caused by the addition of the reinforcement materials.

Figure 3 shows the strengthening efficiencies of our TMCs compared to the values based on previous studies [24–26]. This figure shows that our TiBw has a remarkably high value of \( R \) compared to the results of other
groups [24–26] due to the relatively high $S$ factor of 58. The aspect ratio of TiB whiskers has been reported to be less than 10 [24–27], while maximum aspect ratio of our TiB whiskers is 58 due to significantly reduced diameter, 100 nm of TiBw. This result stems from the control of the growth rate in the transverse direction of the TiBw in the TiBw/Ti–6Al–4V composite, as shown in the insets of Figure 3. It also confirms that the aspect ratio of the TiBw is the main factor that influences the mechanical properties of the TMC when reinforced by TiBw, thus enabling the transfer of a load from a soft matrix to hard reinforcements.

In summary, a TiBw/Ti–6Al–4V composite reinforced by TiBw with a high aspect ratio was fabricated by varying the initial TiB2 powder size. It was found that the TiBw diameter could be one of the dominant factors in the control of the aspect ratio of TiBw. The measured and calculated elastic modulus and the yield strength of the TiBw/Ti–6Al–4V composite suggest the possibility of an effective load transfer from the Ti–6Al–4V matrix to the TiBw. The strengthening efficiency of TMC was also enhanced by TiBw with a high aspect ratio (the TiBw diameter was approximately 100 nm), showing as much as a sixfold increase over the established value. These results demonstrate that increasing the aspect ratio of TiB whiskers should be considered as a key factor in Ti alloys for high-strength Ti-based materials.

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**Figure 3.** Comparison of strengthening efficiencies of TiBw/Ti–6Al–4V composites with TiBw of different aspect ratios.

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