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Effect of aspect ratios of in situ formed TiB whiskers on the mechanical properties of TiB_w/Ti–6Al–4V composites

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Ti alloy matrix composites reinforced with nanosized TiB whiskers (TiB_w/Ti–6Al–4V) were synthesized through an in situ reaction between TiB_2 and Ti–6Al–4V powders during a spark plasma sintering process. The TiB_w/Ti–6Al–4V composites reinforced by whiskers with an aspect ratio of 58 exhibited threefold greater strengthening efficiency compared to those reinforced by whiskers with low aspect ratios. It was determined that the strengthening originates from the high load-bearing capability of TiB whiskers with a diameter of 100 nm formed in situ in a Ti alloy matrix.

Keywords: TiB_w/Ti–6Al–4V composite; Mechanical properties; Aspect ratio; In situ formed TiB whiskers; Spark plasma sintering

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_5Si_3, CrB, B_4C, 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_w), which have a CTE similar to that of the Ti matrix and good chemical stability. However, it is unfortunately difficult to fabricate TiB_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_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_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_w with initially size-controlled TiB_2 powders. TMCs having various aspect ratios of TiB_w were then prepared, and their microstructures and

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mechanical properties were investigated in an effort to clarify the effect of the aspect ratio of TiB_w on the mechanical properties of the TMCs. In particular, TMCs reinforced by relatively thin TiB_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_w with an aspect ratio of 10.

TiB_2 (99%, 3 μm, KOJUNDO) and Ti–6Al–4V (99%, ∼43 μm, Koralco Corporation) powders were used in this investigation. The TiB_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_2 particles were initially controlled by using a planetary milling process for specific milling times to obtain TiB_w with various diameters. Three differently sized TiB_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_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^{-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_w/Ti–6Al–4V composite. The tensile properties of the TiB_w/Ti–6Al–4V composite were determined using an INSTRON 4206 device at a crosshead speed of 0.2 mm min^{-1}.

To synthesize Ti alloys reinforced by TiB_w, TiB_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_2 powders were homogeneously dispersed and embedded in a Ti matrix. The TiB_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_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_w and then stacked in the transverse direction while maintaining the length of the TiB_w. That is, the diameter of the TiB_w decreases as the TiB_2 particle size decreases, leading to a high aspect ratio. Thus, we attempted to use size-reduced initial TiB_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_w.

We controlled the diameter and aspect ratio of the TiB_w as a function of the TiB_2 particle size via a high-energy milling process, as shown in Table 1. As expected, the diameter of the TiB_w increased as the TiB_2 particle size increased. As seen in Table 1, there were no significant differences in the grain sizes or the microstructure of the TiB_w/Ti–6Al–4V matrix composites with different TiB_2 particle sizes. However, only part of the aspect ratio of the TiB_w was increased markedly as the diameter of the TiB_w in the TiB_w/Ti–6Al–4V composite was decreased. Additionally, the aspect ratio was reduced upon the addition of more TiB_2 powder.

Figure 1(b) shows the surface morphology of 1 vol.% TiB_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

Table 1. Aspect ratios of the TiB whiskers synthesized by varying the initial size of TiB_2 powders, grain sizes and relative densities of the TiB_w/Ti–6Al–4V composite with various aspect ratios of TiB_w.

Initial TiB_2 powders		TiB_w/Ti–6Al–4V composite				
		In situ formed TiB whiskers				
Wt.%	Size	Average diameter	Aspect ratio	Vol.%	Grain size	Relative density (%)
0.5	500 nm	100 nm	58	1	6.3 ± 3.1	99
	1 μm	500 nm	38		6.5 ± 3.7	99
	3 μm	1 μm	18		6.6 ± 3.3	99
3	3 μm	1 μm	13	5	6.8 ± 4.1	99

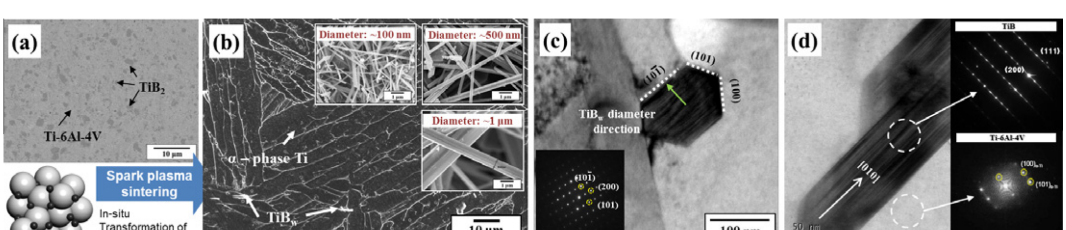

Figure 1. (a) A surface SEM microstructure and a schematic illustration of TiB_2/Ti–6Al–4V composite powders fabricated by a mechanical alloying process. (b) A field emission SEM surface morphology of 1 vol.% TiB_w/Ti–6Al–4V composites with ∼100 nm diameter of TiB_w; the inset image shows the TiB whiskers 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_w in the plane of the diameter and (d) a cross-section of TiB_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 TiB_w. 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 TiB_w and the phases of TiB_w and Ti–6Al–4V, respectively. It was noted that the cross-section of the in situ TiB_w is characterized by (1 0 0), (1 0 1) and $(1 0 \bar{1})$ crystal planes with a hexagonal shape. In addition, the growth in the longitudinal direction of the TiB_w is in the [0 1 0] direction, as reported in earlier studies [17–20].

It was reported that the diameter and length of the TiB_w have quite different growth rates; TiB_w 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 TiB_2 powders at the same amount. Even though the size of the TiB whiskers changed with the size of the TiB_2 particles, we think that the inter-particle spacing between the TiB whiskers is not much different from the inter-particle spacing between the TiB_2 particles in the microstructures. This is because the TiB whiskers are formed in random directions at the TiB_2 particles and the length of the in situ formed TiB whiskers is about 5–10 μm, which is much larger than the TiB_2 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 TiB_w/Ti–6Al–4V composite.

The elastic modulus (E_c) and the yield strength (σ_c) of a TiB_w/Ti–6Al–4V composite with TiB_w of different aspect ratios were measured by tensile testing. The measured values of both E_c and σ_c of the TiB_w/Ti–6Al–4V composite exhibited enhanced behaviors upon increasing the aspect ratio of the TiB whiskers. As shown in Figure 2(a), the measured E_c value of the TiB_w/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.%, the E_c value increases upon an increase in the S value from 18 to 58. The E_c 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 TiB_w/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 σ_c value of the TiB_w/Ti–6Al–4V composite using a generalized shear-lag model [22,23] because the shape of TiB_w is assumed to be cylindrical. We calculated σ_c using the following equation:

$$\sigma_c = V_f \sigma_m \frac{S}{2} + \sigma_m \qquad (1)$$

where V_f is the volume fraction of TiB_w, S is the aspect ratio of the reinforcement (TiB_w), σ_m is the yield strength of the matrix and σ_c is the yield strength of the composite. As shown in Figure 2(b), we plotted the estimated σ_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 σ_c value of TiB_w/Ti–6Al–4V composites reinforced by TiB_w 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 TiB_w enables the strengthening of a TiB_w/Ti–6Al–4V composite. The strengthening efficiency of the TiB_w/Ti–6Al–4V composite can be expressed by the following equation:

$$\sigma = \sigma_m (1 + V_f R) \qquad (2)$$

In this equation, R is the strengthening efficiency of the reinforcement, V_f is the volume fraction of the reinforcement (TiB_w) and σ_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 TiB_w has a remarkably high value of R compared to the results of other

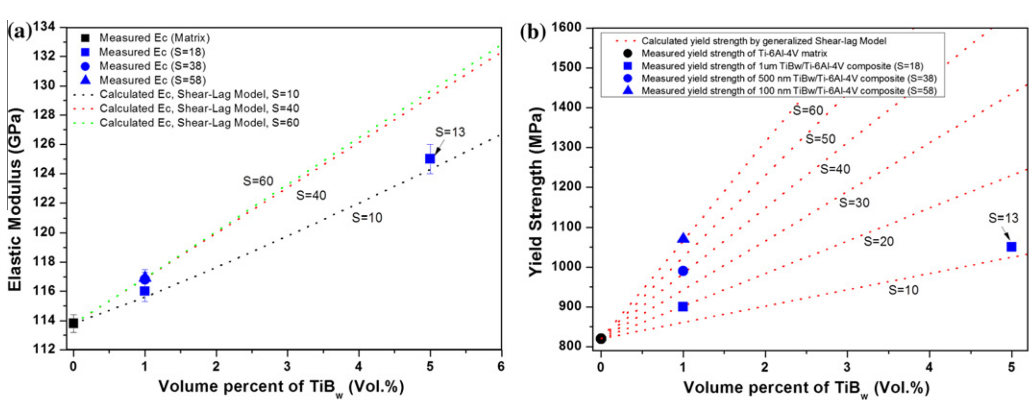

Figure 2. Comparison between the measured and calculated mechanical properties for (a) the elastic moduli of 1 and 5 vol.% TiB_w/Ti–6Al–4V composites with different S of TiB_w and (b) the yield strengths of 1 and 5 vol.% TiB_w/Ti–6Al–4V composites for aspect ratios from 10 to 60 (dotted lines).

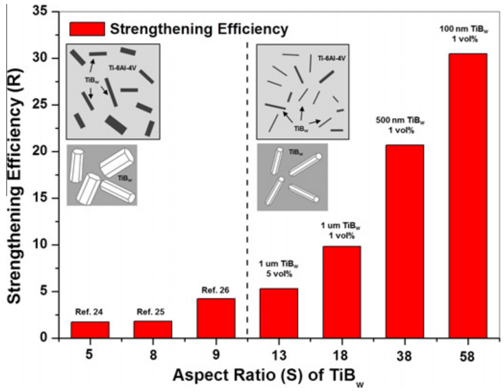

Figure 3. Comparison of strengthening efficiencies of TiB_w/Ti–6Al–4V composites with TiB_w of different aspect ratios.

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 TiB_w. This result stems from the control of the growth rate in the transverse direction of the TiB_w in the TiB_w/Ti–6Al–4V composite, as shown in the insets of Figure 3. It also confirms that the aspect ratio of the TiB_w is the main factor that influences the mechanical properties of the TMC when reinforced by TiB_w, thus enabling the transfer of a load from a soft matrix to hard reinforcements.

In summary, a TiB_w/Ti–6Al–4V composite reinforced by TiB_w with a high aspect ratio was fabricated by varying the initial TiB_2 powder size. It was found that the TiB_w diameter could be one of the dominant factors in the control of the aspect ratio of TiB_w. The measured and calculated elastic modulus and the yield strength of the TiB_w/Ti–6Al–4V composite suggest the possibility of an effective load transfer from the Ti–6Al–4V matrix to the TiB_w. The strengthening efficiency of TMC was also enhanced by TiB_w with a high aspect ratio (the TiB_w 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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