EFFECT OF REINFORCEMENT CONTENT ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF IN SITU (TiB_W+TiC_P)/(Ti-4.0Fe-7.3Mo-5.2Cr) COMPOSITE

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Abstract
Titanium alloys have a wide application as its good toughness and strength, but these alloys have relative low abrasion resistance. However, this short coming can be addressed by fabricating titanium matrix composites. (TiB_w+TiC_p)/(Ti-4.0Fe-7.3Mo-5.2Cr), the composites with TiB:TiC=1:1 but different reinforcement content have been prepared by using in situ reaction between B_4C, C, Cr_3C_2 and titanium powders with the changing the proportions. The mixtures were hot pressed at 1300 ℃, under a pressure of 20 MPa for 1 hour in Ar atmosphere and both the microstructure and mechanical properties of the composites have been investigated. XRD and SEM results show that the reinforcement content can affect both the matrix and reinforcing phase. Additionally, the reinforcement content can also influence the morphology of in situ formed TiB_w and TiC_p reinforcements.

1 Introduction
Titanium alloys are proven to be potentially very suitable materials as structure part for load bearing application because of the low density, high elastic modulus, high specific strength and good high temperature creep resistance, [1-5]. However, those alloys exhibit poor wear resistance which constraint their further application as transport materials. This disadvantage can be addressed by producing composites with the ceramic phase. According to Westwood's study, [6], high hardness particulate reinforcement can enhance the strength, elastic reinforcement can improve the toughness, and whiskers can help to improve the creep resistance. Therefore, a TiC and TiB mix reinforced titanium alloy should possess a very good combination of strength and abrasion resistance.

Many techniques have been investigated for preparing Titanium alloys matrix composite, such as powder metallurgy, diffusion bonding, squeeze casting, spray casting and chemical vapor deposition. Among these techniques, Powder metallurgy is the most popular method for fabricating titanium alloys composite, and the particulate and whiskers reinforced composites were produced by applying in-situ technology in our study. Compare with no-in situ technology, it has prominent advantages: the matrix alloy and reinforcement are thermodynamic stability, not easy to destroy while serving in a high temperature environment; the size of reinforcement is small and distributes evenly, so the composites can get excellent mechanical properties; the high bond strength interface between reinforcements and matrix is clean; what's more the production process is more safer for researchers, [7-8].

Interest in introducing Cr_3C_2 into the composite as raw material is for a variety of reasons, not least of which is possibility to react with titanium for forming TiC. However, adding Cr element into the matrix alloy can enhance the strength and abrasion resistance of the matrix effectively, [9], meanwhile, due to the theory strength of titanium calculated Mo equivalent, [12], the strength of the matrix alloy should increase which may help to the wear resistance, as would be expected.

$$\sigma_b^{calculated} = 235 + 60[Al]_{equivalent}^{strength} + 50[Mo]_{equivalent}^{strength} \quad (1)$$

The work reported here is based on previous studies, utilizing cheap materials and preparation methods to produce the titanium matrix composite with high strength and wear resistance. (TiB_w+TiC_p)/(Ti-4.0Fe-7.3Mo-5.2Cr) composites with TiB:TiC=1:1 was produced by hot pressing sintering using Ti-B_4C-Cr_3C_2-C-Fe-Mo as raw material. Microstructure and mechanical properties of the composites have been investigated, in order to find out the effect of content of TiB_w+TiC_p on microstructure for obtaining a better understanding on the strengthening mechanisms and abrasion resistance.

2 Materials and testing methods

2.1 Experiment design

The nominal matrix alloy (Ti-4.0Fe-7.3Mo-5.2Cr) was designed as the matrix alloy base on the new Timetal-LCB alloy (Ti-4.5Fe-6.8Mo-1.5Al), using Fe powder, Mo powder, Ti powder, B_4C powder, Cr_3C_2 powder and graphite as raw materials. According to the calculated Mo equivalent, [12], the theory strength of the matrix can reach to 900MPa.
As reported in recent references, three useful self-propagating reactions can be found and listed in equations (2), (3), [9-10],and (4), [11], as below:

$$5Ti + B_4C = 4TiB + TiC \quad (2)$$

$$Ti + C = TiC \quad (3)$$

$$2Ti + Cr_3C_2 = 2TiC + 3Cr \quad (4)$$

Therefore, the TiB and TiC molar ratio can be ensured to 1 : 1 by controlling the adding contain of graphite B_4C and Cr_3C_2, and the following reaction can be obtained:

$$(5 + x + 2y + z)Ti + B_4C + xC + yCr_3C_2 = 4TiB + (1 + x + 2y)TiC + zTi + 3yCr \quad (5)$$

Sample code	TiB_w+TiC_p content	TiB:TiC mole ratio	Raw materials [wt%] Ti	Fe	Mo	B_4C	Cr_3C_2	C
10TBC4	10vol%	1：1	83.85	3.44	6.27	1.10	5.38	0.00
15TBC5	15vol%	1：1	83.66	3.27	5.96	1.62	5.12	0.37
20TBC6	20vol%	1：1	83.56	3.07	5.61	2.22	4.70	0.83

Table 1. Chemical compositions of the samples used

According to equation (5), the molar ratio of TiB and TiC is 4 : (*1+x+2y*), based on this the reinforcement content can be produced, as would be expected.

2.2 Material processing

For preparing $(TiB_w+TiC_p)/(Ti\text{-}4.0Fe\text{-}7.3Mo\text{-}5.2Cr)$ MMCs, the raw materials were titanium powder (99.5%, average particle size, 10 μm), B_4C powder (98%, average particle size, 3.5 μm), graphite powder (99.95%, average particle size, 200 nm), Cr_3C_2 powder (99.5%, average particle size, 2-3 μm), and other alloying elements such as Fe, Mo. The volume percentage of reinforcements is 10%, 15% and 20%, respectively, as listed in Table 1. Raw powders were sealed in the glove box and mixed by ball mill, setting the speed of ball milling to 120 r/min, mixing 24 h with the ball-to-powder weight ratio is 1:10. In order to ensure the chemical homogeneity of the composites, the mixed powders were hot pressing sintering at 1300 ℃, with a pressure of 20 MPa for 1 hour in Ar atmosphere.

2.3 Microstructure examination

Samples for SEM were cut from the products, and prepared using conventional techniques of grinding and mechanical polishing. Phase identification of the composites was performed by a Philipx'pert-ray diffraction (CuKα, 4 °/min). The character of reinforcements and finer details of the microstructure were carried out using a Tecnai G2 F30 transmission electron microcope. For study the mechanical properties of the composites under ambient condition, three point bending and fracture toughness sample were machined from hot press sintered bulk with the size of 3 mm × 4 mm × 40 mm and 2 mm × 4 mm × 20 mm, then they were tested on Instron-1186 with the strain rate of 0.5 mm/min and 0.05 mm/min, respectively.

3 Results and discussion

3.1 XRD analysis

The XRD pattern analysis results of the composites are shown in Figure 1. TiC and TiB are found in the composites, indicating that the original powder B_4C, Cr_3C_2 and C have been reacted completely. The composite is comprised of the α-Ti and β-Ti phase. And as the increase in reinforcement content, the content of β-Ti phase increases, while TiC and TiB peak intensity continues to increase.

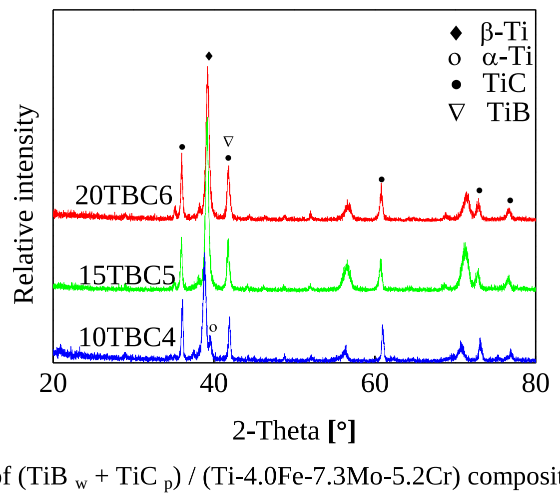

Figure 1. XRD patterns of $(TiB_w + TiC_p)$ / (Ti-4.0Fe-7.3Mo-5.2Cr) composite with different reinforcement content

3.2 MICROSTRUCTURE ANALYSIS

Figure 2 shows the SEM morphology of the (TiB_w+TiC_p)/ (Ti-4.0Fe-7.3Mo-5.2Cr) composites with different content of the reinforcement. Two kinds of reinforcement can be found in the composite, particles and long rod (needle) whisker. They distributes in the matrix evenly. With the increasing of the reinforcement content, the aspect ratio of whisker-like reinforcement reduced continuously, and the size of the reinforcement decreased at the same time.

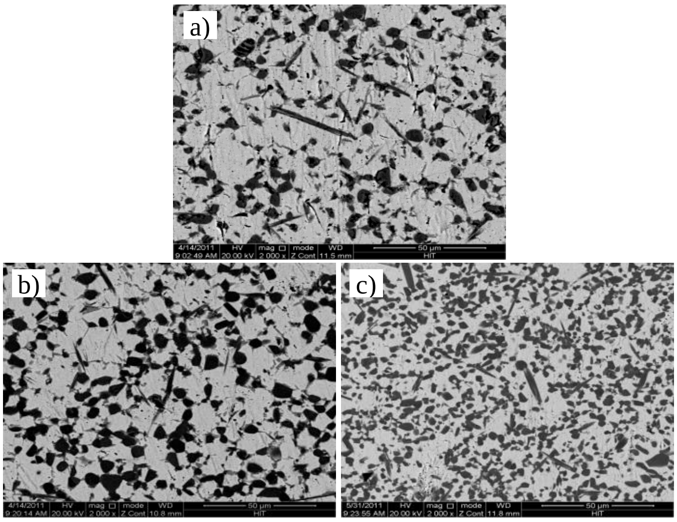

Figure 2. SEM morphology of the (TiB_w+TiC_p)/ (Ti-4.0Fe-7.3Mo-5.2Cr) composites with different content of the reinforcement
a) 10TBC4 b) 15TBC5 c) 20TBC6

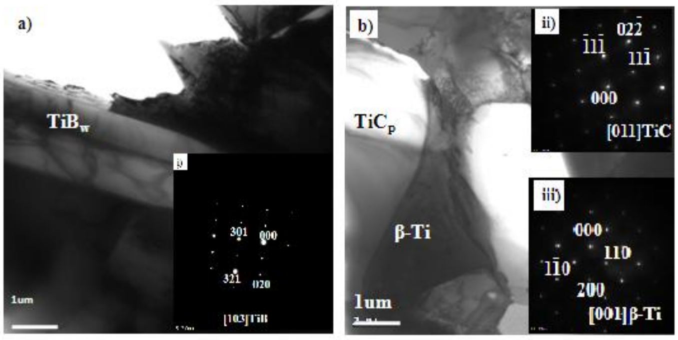

Figure 3. TEM images and diffraction spots of the composites
a) TiB whisker b) TiC particulate, β-Ti alloy and their diffraction spots (i), (ii) and (iii) respectively

Figure 3 shows the TEM and diffraction spots of reinforcements and matrix alloys. Similar with the SEM results, particle and whisker reinforcement can be found from the Fig. , as expected. Hence, the diffraction spots show significant difference between reinforcements and matrix alloy. Therefore, we can easily get that TiC is particulate, TiB is whisker-like reinforcement and the matrix is β-Ti by marking the diffraction spots TiB[-103], TiC[011] and Ti[001], respectively.

Through XRD, SEM and TEM morphology analysis, it can be found that the reinforcement can impact the shape of TiB and TiC directly. Remain the matrix alloy unchanged, with the increasing of the content of reinforcement formed by in situ reaction, the aspect ratio of TiB whisker decreased. This is mainly due to the atom diffusion in the in situ reaction process. Rising the concentration of one kind atom singly will restrain the diffusion of other kinds of atoms, especially, the atom with smaller molecular size like graphite. The high concentration of graphite inhibits the diffusion of B_4C, so the in situ reaction can only occur near the B_4C molecular, and can't provide adequate response atoms to lead the TiB grow along the [010] direction as the long rod-like whisker.

3.3 Mechanical propertie

In order to study the effect of reinforcement content on composite performance, flexural strength, Young's modulus, fracture toughness and hardness of the composite had been texted.

3.3.1 Flexural strength and fracture toughness

The Flexural strength of the (TiB_w+TiC_p)/(Ti-4.0Fe-7.3Mo-5.2Cr) composites with different content of the reinforcement show in figure 4, where the flexural strength first increase and then decrease can be seen, with the same process conditions and an increase in reinforcement content. And it indicated that when the reinforcement content reach to 15 vol.%, the composite get the highest flexural strength which is 1070.5 MPa.

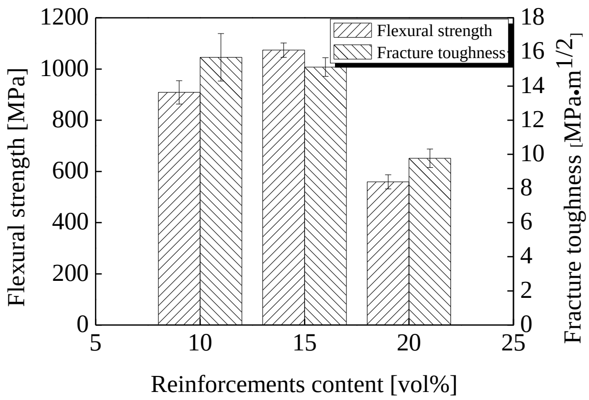

Figure 4. Flexural strength and fracture toughness of the (TiB_w+TiC_p)/ (Ti-4.0Fe-7.3Mo-5.2Cr) composites with different content of the reinforcement

As shown in Figure 4, the changes in fracture toughness mainly due to the number of TiB whisker with big aspect ratio which can play an efficiency role on strengthen decreased. The strengthening effect of the whisker reinforcement is determined by the aspect ratio of the whisker, only when the aspect ratio is greater than the critical aspect ratio, the whisker can play an efficiency role on load enhancement. The critical aspect ratio of whisker is calculated by type (6).

$$\lambda=l_c/d=\sigma_f/2\tau_s \tag{6}$$

Where λ is the critical aspect ratio; τ_s is the interfacial shear strength between the matrix and short fiber, can be instead by the matrix shear strength (MPa); σ_f is whisker tensile strength (MPa).

As to TiB whisker, it should be 3500 MPa, [13-15]. By calculating, the critical aspect ratio of TiB whisker in these composites is about 3.2.

When the reinforcement content is less than 15 vol.%, the aspect ratio of TiB whisker is bigger than the critical aspect ratio, so it can play a good toughening effect, making the flexural strength and fracture toughness improved. But when the content of reinforcement reach to 20 vol.%, the shape of TiB change to short stick-like whisker, and its aspect ratio is smaller than the critical one, so the composite is insufficient to the load, then strength and toughness decline significantly.

3.3.2 Young's Modulus

Ordinarily, the Young's modulus of titanium alloys is about 107GPa, but by adding ceramic reinforcement, the Young's modulus become much higher than this value. Figure 5 shows the Young's modulus of the (TiB_w+TiC_p)/ (Ti-4.0Fe-7.3Mo-5.2Cr) composites with different content of the reinforcement. While the reinforcement content increases from 10% to 20%, the Young's modulus increases from 153.7 GPa to 163.2 GPa.

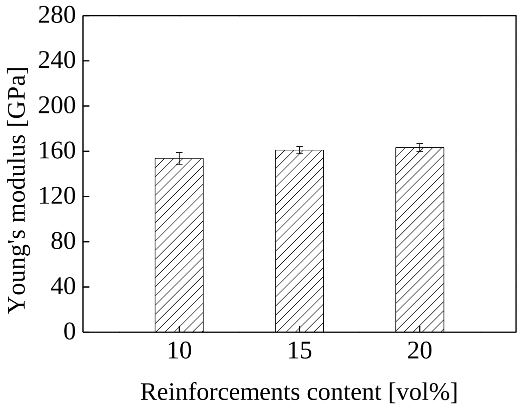

Figure 5. Young's modulus of the (TiB_w+TiC_p)/ (Ti-4.0Fe-7.3Mo-5.2Cr) composites with different content of the reinforcement

The Young's modulus and hardness of the composites is, and the Young's modulus is similar to satisfy the formula (7), mainly determined by the reinforcement content. It increases subsequently, with the increase in content of reinforcements.

$$E = (V_1 E_1 + V_2 E_2) / V \qquad (7)$$

3.3.3 Hardness

Figure 6 shows that with the increasing of reinforcement volume fracture, the Vickers hardness of the composite significantly increased, indicating that adding ceramic reinforcement can improve the hardness of the composite. As not only the matrix but also the reinforcement can play a role on resisting the hard object carving into the composite, with the increasing of reinforcement content, the number of high-hardness ceramics increased, therefore the hardness increases steadily from 609.2 kg mm^{-2} to 748.6 kg mm^{-2}.

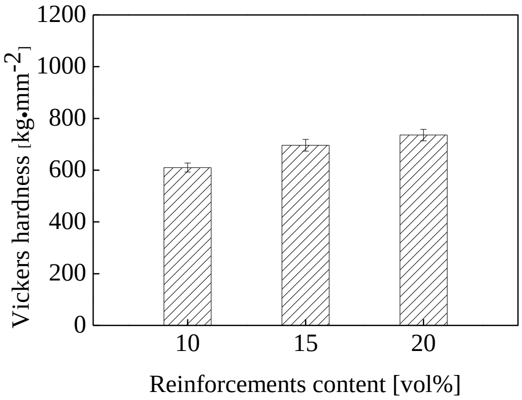

Figure 6. Vickers hardness of the (TiB_w+TiC_p)/ (Ti-4.0Fe-7.3Mo-5.2Cr) composites with different content of the reinforcement

4 Conclusions

In this study, the (TiB_w+TiC_p)/ (Ti-4.0Fe-7.3Mo-5.2Cr) composites with different content of the reinforcement are fabricated by hot press sintering using the reactions between the raw materials. With the increase of reinforcement content formed by in situ reaction, both the aspect ratio of TiB whisker and the size of TiC particle decreases. The flexural strength and fracture toughness of the composites first increase and then decrease. While the in situ formed TiB and TiC can play a role on dislocation strengthening for the matrix and a composite strengthening for the composite, but too much reinforcement also lead to the brittleness of composite. Additionally, when the reinforcement content reach to 15 vol.%, the composite can get excellent mechanical properties, the flexural strength, fracture toughness, Young's modulus and hardness of that reach to 1070.5 MPa, 15.11 MPa $m^{1/2}$, 160.9 GPa and 696.4 kg mm^{-2}, respectively.

Acknowledgements

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