In Situ Synthesis of TiB/Ti6Al4V Composites Reinforced with Nano TiB through SPS

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Titanium matrix composites reinforced with TiB whiskers were in situ synthesized by spark plasma sintering (SPS) at a temperature range of 1173–1473 K, using a mixture of 6.2 mass% TiB₂, 4.1 mass% Ti, and 89.7 mass% Ti6Al4V powders. The in-situ synthesis mechanism and the effect of sintering temperature on the sintering microstructure were investigated. The results show that an increase of the sintering temperature causes the relative densities of the composites to increase and the reaction between Ti and TiB₂ to be more complete. Nano-sized TiB reinforcements with a diameter of around 80 nm and fine-grained matrix with an average grain size of 12 µm are obtained after SPSed at 1373 K. Clean and perfect TiB/matrix interfaces without debonding or cracks are obtained during SPS process. Low sintering temperature and short sintering time are believed to be the main reasons for the improved fine-grained microstructure. [doi:10.2320/matertrans.M2014347]

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1. Introduction

Titanium matrix composites (TMCs), with the characteristics of high special strength, high temperature durability, excellent wear resistance and high special stiffness, have been considered as the optimal candidate material among the fields of military applications, aerospace and commercial automotive.¹⁻⁴ Ti6Al4V is a typical α/β titanium alloy, which has been widely used as matrix of TMCs in recent years due to its prior mechanical properties. TiB₂, TiB, TiC, SiC, and Al₂O₃ have been employed to prepare TMCs by various processing approaches, such as casting, powder metallurgy (P/M), self-propagation high temperature synthesis (SHS) and mechanical alloying (MA).⁵⁻⁸ Among these reinforcements, TiB has the similar thermal expansion coefficients (7.2 x 10⁻⁶ K⁻¹) with Ti (8.2 x 10⁻⁶ K⁻¹). TiB reinforcement has the prior properties of high hardness, good wear, and excellent chemical stability, which makes it an outstanding reinforcement of TMCs.⁹,¹⁰ Moreover, TiB is the product of the reaction between Ti and TiB₂, thus it can be in situ synthesized in the TMCs, and provides a clean interface between Ti matrix and TiB reinforcements without any impurity. The flawless interfacial bonding of TiB and matrix improves the mechanical properties of the TMCs remarkably.¹¹⁻¹³

SPS is an advanced sinter process, and can fabricate nanocrystalline materials that are difficult to be prepared using common methods.¹⁴⁻¹⁶ SPS is based on electrical current activation and produces plasma in the graphite die. The pressure is loaded on the sample during the whole SPS process, which enables the sinter process to proceed at a low temperature, with short heating, holding and cooling time. Thus, the grain growth is prohibited and finally forms a fine microstructure.¹⁷⁻²⁰

Considerable research has been carried out on the synthesis of TiB/Ti composites by casting²¹ and powder metallurgy (P/M).²²,²³ but the results have been unsatisfactory due to the coarse microstructure of the matrix and TiB reinforcements. Little data is available on the synthesis of TiB/Ti6Al4V by the SPS process. Therefore, this paper studies the TiB/Ti6Al4V composites in-situ synthesized by the SPS method, the in-situ reaction mechanism and also the effects of sintering temperature on the microstructure are discussed.

2. Experimental Procedures

2.1 Starting powders

Composition of Ti6Al4V+10 vol.% TiB was selected in the present study because the composite has superior mechanical properties.²⁴ For preparing the TiB/Ti6Al4V composite, spherical Ti6Al4V powder with an average particle size of 11 µm, irregular Ti powder with an average particle size of 39 µm and TiB₂ powder with an average particle size of 3.8 µm were used. The particle sizes of these powders are uneven in order to stack densely and gain high density during SPS process. TiB was in situ synthesized by the chemical reaction between Ti and TiB₂ during the SPS process. A mixture of the composite was prepared by milling 89.7 mass% Ti6Al4V, 4.1 mass% Ti and 6.2 mass% TiB₂ powders in a planetary mill for 2 h at milling rotation speed of 400 rpm, using ethanol and agate balls as a milling medium. The weight ratio of balls to powder was fixed to 6 : 1. The resultant slurry was dried in vacuum evaporator.

2.2 SPS process

The powder mixture was sintered on a SPS system (HP D25/3 type, FCT Corporation, Germany). The SPS process was performed using a cylindrical graphite die with external and internal diameters of 40 mm and 20 mm respectively. The specimens were sintered at temperatures of 1173 K, 1273 K, 1373 K, and 1473 K with a heating rate of 100 K/min and a holding time of 5 min. The sintering pressure was 40 MPa. After sintering, the pressure was released and the sample was allowed to cool within the sintering chamber.
2.3 Characterization tests
A layer of about 1 mm was removed from the specimen by using an electro discharge cutting machine, so as to avoid any effect of impurity from graphite die during the microstructure and density test. The bulk density was determined by the Archimedes method. The theoretical density of the composites is considered as 4.51 g/cm$^3$. Phase identification was performed using X-ray diffraction (XRD, D/max 2550, Japan) analysis. Microstructure investigation of the sintered composites was carried out using a Scanning Electron Microscope (SEM, Nova Nano SEM230, America) and Transmission Electron Microscopy (TEM, JEM-2100F, Japan). The interface of the reinforcements and matrix was studied by High Resolution Electron Microscopy (HREM, JEM-2100F, Japan).

3. Results and Discussion

3.1 Densification
Figure 1 presents the densification curve of the TiB/Ti6Al4V composites during SPS process. Densification starts at about 773 K. The reason for this densification is the uniaxial compression during the sintering process, which causes a particle rearrangement. With the increase of sintering temperature and pressure (especially after 873 K), the densification quickens due to the plastic deformation of the powder mixture. When the temperature reaches the sintering temperature and pressure (especially after 873 K), particle rearrangement occurs due to the plastic deformation of the powder mixture. The densification mechanism changes from the plastic deformation to the creep deformation.\(^{(1)}\)

Figure 2 indicates the influence of the sintering temperature on the relative density of the SPSed TiB/Ti6Al4V composites. Nearly no diffraction peak of TiB$_2$ is observed that in the present study, which is probably due to the particle size of the TiB$_2$ powder (30 µm) being bigger than that in the

The current and spark in the graphite die could break the surface oxide layers of the particles and thus increase the chemical reaction and improve the relative density. In addition, vacancies formed during reaction of Ti and TiB$_2$ can be filled with Ti atoms under the pressure, which also has a positive effect on the relative density of the SPS materials.\(^{(17)}\)

3.2 Reaction products
In the Ti-B binary system, the following reactions can take place during sintering process:\(^{(10)}\)

\[
\begin{align*}
\text{Ti} + \text{TiB}_2 & = 2\text{TiB} \quad (1) \\
\text{Ti} + \text{B} & = \text{TiB} \quad (2) \\
\text{Ti} + 2\text{B} & = \text{TiB}_2 \quad (3)
\end{align*}
\]

The Gibbs free energy change values $\Delta G$ of reactions (1)–(3) have been calculated to $-6.3$ kJ/mol, $-157$ kJ/mol and $-308$ kJ/mol, respectively.\(^{(10)}\) The result shows that the $\Delta G$ values of the above reactions are negative, indicating that all three reactions can take place under certain conditions. Although $\Delta G$ of reaction (3) is the most negative, Ti and TiB$_2$ can further react to form TiB due to the negative value of the free energy of reaction (1). Therefore, TiB$_2$ will be converted to TiB if there is enough content of Ti in the reaction zone.

Figure 3 shows the X-ray diffraction patterns of the TiB/Ti6Al4V composites sintered at temperature range of 1173–1473 K. Obviously, the phases of the specimens change while increasing the sintering temperature. The diffraction peaks of $\alpha$-Ti and $\beta$-Ti are present in all these spectra for the composites. Nearly no diffraction peak of TiB$_2$ is observed in the XRD spectra for the composite sintered at 1373 K, indicating that the chemical reaction shown in eq. (1) completes at this temperature. Wei \textit{et al.}\(^{(9)}\) studied the TiB-Ti composites synthesized by the SPS process and reported that the initial and complete reaction temperatures between Ti and TiB$_2$ are approximately 1073 K and 1423 K at a heating rate of 100 K/min. The complete temperature is higher than that in the present study, which is probably due to the particle size of the TiB$_2$ powder (30 µm) being bigger than that in the

![Figure 1](image1.png) Displacement versus time for the SPS process.

![Figure 2](image2.png) Influence of the sintering temperature on the relative density of the SPSed TiB/Ti6Al4V composites.

![Figure 3](image3.png) X-ray diffraction patterns of the TiB/Ti6Al4V composites.
present study (3.8 µm). If the particles are small, more contact points for the neck formation are available, and the diffusion paths become short. Furthermore, the driving force to reduce the particle surface is high. Therefore, the reaction speed is faster and the complete reaction temperature is lower.

The relative volume fractions of the composition phases can be computed from the integrated intensities of the selected peaks in the X-ray diffraction pattern by the direct comparison method. The results indicate that the volume fraction of TiB in the composite sintered at 1473 K is about 11%, which is close to the theoretical ingredient of the TiB/Ti6Al4V composite synthesized from the mixture of 6.2 mass% TiB₂, 4.1 mass% Ti and 89.7 mass% Ti powders.

3.3 Microstructure characteristics

Figure 4 shows the SEM microstructures of the TiB/Ti6Al4V composites synthesized by the SPS process at different sintering temperatures. With increasing sintering temperature from 1173 K to 1473 K, more and more TiB whiskers are synthesized through the in-situ reaction. Because TiB phases adopt a B2 crystal structure and the planes with a higher density of strong bonds tend to grow at a higher rate, TiB should grow along the [010] direction and develop a needle-shaped or rod-like morphology. As illustrated in Fig. 4(c) and (d), the TiB phases have a needle-shaped or rod-like morphology with a high aspect ratio and are uniformly distributed within the matrix. The Ti6Al4V matrix consists of fine-grained α phase (grey) and network β phase (white). The average grain size of the matrix of the composite sintered at 1373 K is about 12 µm, and the grain size does not change dramatically with the change of sintering temperature, this is probably caused by the

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existence of TiB reinforcements. Large pores can be observed in the composites sintered at 1173 K and 1273 K, and the porosity of the composites decreases with increasing sintering temperatures. Some unreacted TiB$_2$ particles are detected in the composites sintered at 1173 K and 1273 K, indicating that the chemical reaction between Ti6Al4V and TiB$_2$ was not completed at these sintering temperatures. Few pores can be detected in the composites sintered at 1373 K and 1473 K, suggesting that the TiB/Ti6Al4V composite sintered at this temperature is nearly fully dense.

Figure 5 shows the TEM images of the TiB/Ti6Al4V composite sintered at 1373 K. The TiB is present in the form of fine needles (Fig. 5(a)), and the average diameter of the TiB is about 80 nm (Fig. 5(a), (b) and (c)). Figure 5(d) shows a HREM image of the composite. It is shown that the interface between the in-situ TiB and matrix is clean and perfect, no flaws such as debonding or cracks, can be observed around the interface zone. It is a typical interface formed during an in-situ reaction and a high bonding force can be expected. Gorsse et al.\cite{28} and Radhakrishna et al.\cite{29} prepared the TiB/Ti6Al4V composites by traditional P/M method and obtained needle TiB reinforcements with a diameter of about 8 µm and a matrix with an average grain size of about 35 µm when the sintering is conducted at 1573 K for 6h. Radhakrishna et al.\cite{30} studied the microstructure of TiB/Ti6Al4V composites prepared by hot pressing at 1623 K for 1h and found that the size of the TiB reinforcements is around 3 µm. Banerjee et al.\cite{31} and Tamirisakandala et al.\cite{32} reported that, for the casted TiB/Ti6Al4V composites, the diameter of TiB and the grain size of the matrix are usually in the range of 5–10 µm and 30–50 µm, respectively. The above results indicate that both the particle size and matrix grain size of the TiB/Ti6Al4V composite obtained through the SPS are much finer than that of the TiB/Ti6Al4V composites fabricated by traditional P/M and cast methods. The SPS causes the fine microstructure by its nature. On the one hand, the sintering temperature is much lower than that used in traditional P/M process; on the other hand, under the influence of the pressure and current, the sintering time and the reaction time are much shorter than that in the traditional P/M process. Therefore, the TiB reinforcements and the Ti6Al4V matrix are unable to coarsen during the SPS process, and a fine microstructure of the TiB/Ti6Al4V composites can be preserved.

4. Conclusions

Titanium matrix composites reinforced with nano-TiB whiskers were in situ synthesized by spark plasma sintering (SPS). The in-situ synthesis mechanism and the effect of sintering temperature on the sintering microstructure were investigated. The following major conclusions are drawn from this study:

(1) Increasing the sintering temperature causes the relative density of the composite to increase and the reaction
between Ti and TiB₂ to be more complete. The complete reaction temperature during the SPS process is 1373 K.

(2) Nano-sized TiB reinforcements with a diameter of around 80 nm and a fine-grained matrix with average grain size of 12 µm are obtained during SPS sintering at 1373 K. A low sintering temperature and a short sintering time are believed to be the main reason for the improved fine microstructure.

(3) Clean and perfect TiB/matrix interfaces without debonding or cracks are obtained during SPS process.

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