Materials Research Express

PAPER

Influence of the sintering temperature on the microstructure, mechanical properties and densification characteristics of (TiB + TiC)/TC4 composite

Zheng-Yang Hu1,* , Hai-Chun Peng1, Zhao-Hui Zhang2,3 , Peng Song1, Ming Chen1, Yu-Sheng Ding1, Yue-Ying Liang1 and Shao-min Li1

1 Aerospace Institute of Advanced Materials & Processing Technology, Beijing 100074, People’s Republic of China
2 School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, People’s Republic of China
3 National Key Laboratory of Science and Technology on Materials Under Shock and Impact, Beijing 100081, People’s Republic of China
* Author to whom any correspondence should be addressed.

E-mail: Huzy_job@163.com

Keywords: titanium matrix composite, spark plasma sintering, densification mechanism, mechanical property

Abstract

A hybrid of TiB whiskers and TiC particles reinforced TC4 matrix composites were in situ synthesized by spark plasma sintering (SPS) using a TC4-0.6wt.% B4C powder mixture at temperatures range from 550 °C to 1150 °C. The effect of sintering temperature on microstructure, grain size, mechanical properties and densification process of the (TiB + TiC)/ TC4 matrix composites were investigated. The composite sintered at 1050 °C has the highest tensile strength (1129.0 MPa), yield strength (1077.8 MPa) and plasticity (7.1%). The aspect ratio of TiB whiskers increases almost linearly below 1050 °C and its highest value is 33.2. The grain size of TiC increases with the increase of sintering temperature, and rapid growth occurs in the range of 850 °C to 950 °C. The composite sintered body appears four shrinkage stages before applying sintering pressure. The corresponding peak temperatures are 663 °C, 758 °C, 840 °C and 994 °C, respectively.

1. Introduction

As a kind of advanced structural material, titanium matrix composites (TMCs) has many attractive properties, such as low density (4.2–4.9 g/cm³), high service temperature (even reaches 600 °C to 800 °C), excellent chemical resistance and excellent biocompatibility [1–4]. The combination of such properties offers a potential 50% weight savings compared to steel and nickel-based superalloys, and makes them an ideal candidate for chemical, aerospace, automotive, lightweight armors and biomedical applications [5, 6].

Among many possible reinforcements, TiB whiskers and TiC particles have been unanimously considered as the best reinforcements, due to their desirable modulus (TiB 425–480 GPa, TiC 440 GPa), hardness (TiB 32 GPa, TiC 27 GPa), good thermodynamic stability and similar coefficient of thermal expansion (CTE, TiB 8.60 × 10⁻⁶ K⁻¹, TiC (6.52–7.15)×10⁻⁶ K⁻¹) with titanium (8.8 × 10⁻⁶ K⁻¹) [7, 8]. (TiB + TiC)/TMCs were successfully prepared using different methods like casting, laser melting, hot pressure and so on. Among these methods, spark plasma sintering (SPS) has attracted much attention as a novel and rapid densification method, which endows (TiB + TiC)/TMCs with desirable properties and high forming efficiency [9–11].

N Singh et al studied the synergistic effect of TiC particles and TiB whiskers reinforcement on titanium matrix composites fabricated by SPS technique at a temperature of 1200 °C for 5 min [12]. A further refinement in microstructure was observed in (0.05B and 0.1B) / (Ti64 + 3TiC) system. The optimum yield strength and average coefficient of friction of (0.1B + 3TiC)/Ti64 are 1288 ± 55 MPa and 1.04, respectively. M. Ozerv et al investigated the mechanical behavior and microstructural response of the Ti/TiB composite using SPS [13]. A higher fraction of unreacted TiB₂ and finer TiB whiskers were observed after sintering at 850 °C. The composite
sintered at 1000 °C showed greater strength at low deformation temperatures and deformed without cracks in contrast to the composite sintered in the top of the α phase field.

It is obvious that all properties of the (TiB + TiC)/TMCs are dependent on their microstructure and, thus, on the sintering conditions. One of the most important parameters is the sintering temperature [14]. The dual thermal effects of Joule heat and plasma in SPS will affect the shrinkage rate of the sintered sample, the densification and in situ reaction process, the growth of the reinforcing phase, and the formation and growth of the sintering neck [15, 16]. Besides, the low-density reactants (B4C or carbon) will react with the matrix powder during the in situ sintering process, resulting in relatively high density TiB (4.50 g cm−3) and TiC (4.92 g/cm3) phases [3, 17]. Therefore, the sintering process will be accompanied by a certain degree of volume shrinkage, and it is easy to form local micropores, which complicates the whole densification process. However, the effect of sintering temperature on in situ reaction, reinforcements growth, mechanical properties and densification process of the (TiB + TiC)/TMCs during the SPS process has not yet been fully explored.

Therefore, the current work was focused on determining the microstructure evolution, relative density, mechanical properties and shrinkage characteristics of (TiB + TiC)/TC4 composites produced by SPS at temperatures range from 550 °C to 1150 °C corresponding to either the α or the β phase fields of the titanium matrix.

2. Experiment

TC4 (Ti-6Al-4V, 99.8%, 26.1 μm, Mengtai Powder Business Department) and B4C powders (99% purity, 5 μm, High Purity Chemical Laboratory Co., Ltd) powders were used in this work. Mixtures contained B4C concentration of 0.6wt.% was milled in a planetary (60 min, 300 rpm). The milling process was performed using quartz balls (10 mm) with the ball-to-powder weight ratio of 4:1. The average particle size of the composite powders obtained by mechanical milling is 26.6 μm, as shown in figure S1 (available online at stacks.iop.org/MRX/8/126517/mmedia).

The Ti-6Al-4V powder and mixtures were sintered into bulks at temperatures of 550 °C, 650 °C, 750 °C, 850 °C, 950 °C, 1050 °C and 1150 °C with a heating rate of 100 °C/min for 5 min in vacuum (<5 Pa). DR SINTER type SPS-3.20 equipment (Sojitz Machinery Corporation, Tokyo, Japan) with pulse duration of 3.3 ms and a current on-off ratio of 12:2 was used in this procedure. Applied initial and holding (sintering) compressive pressure level was 1 MPa and 40 MPa, respectively. The cooling rate is about 120 °C/min (above 650 °C). The diameter and height of the bulk SPSed samples are 30 mm and 15 mm, respectively.

The as-sintered sample was machined into tensile test samples with a gauge length of 10.0 mm, width of 2.0 mm and thickness of 2.0 mm. Tensile-properties were conducted via Instron 5848 Micro-tester (room-temperature, 10−3s−1). To ensure repeatability, each value is reported as an average of four measurements. Phase-evolution was evaluated by X-ray diffraction analysis (XRD, X’Pert PRO-MPD, 40 mA, 0.02°/s) using Cu-Kα radiation (1.54 Å). Scanning-electron-microscope (SEM, Hitachi S-4800N) and transmission-electron-microscope (TEM, Tecnai G2 F20, 200 kV) were used for observation of microstructures. The diameter of SEM

![Figure 1. X-ray diffraction patterns of composites prepared at different sintering temperatures.](image-url)
and TEM specimens are 5 mm and 3 mm, respectively. Grain-, particle- and whisker- sizes were measured using Image-Pro-Plus software. The actual density of as-sintered sample was measured by Archimedes drainage method. The theoretical density of the as-sintered composite is 4.503 g/cm³. The relative density is calculated by the quotient of actual density and theoretical density.

3. Results

3.1. Phase identification

The XRD patterns of the as-sintered samples at different sintering temperatures are presented in figure 1. The pdf reference codes (ICDD database) of B₄C, TiB, TiC, TiB₂, α-Ti, and β-Ti are 00-035-0798, 01-089-3922, 03-065-0966, 00-006-0528, 00-001-1198 and 00-044-1288, respectively. The calculated volume fraction of TiB and TiC is 2.53vol. % and 0.63 vol. %. Since the reinforcement concentration is quite low, some peaks for reaction products are not obvious in the x-ray diffraction patterns. Therefore, the XRD data were merely used to qualitatively analyze the phase composition of the whole sample.

The results show that there are obvious (003)ₐₐ₄C and (021)ₐₔ₄C peaks in the samples at 550 °C and 650 °C. As the temperature rises to 750 °C, the intensity of the B₄C peak in the sample decreases rapidly, and the (111)ₐₐ₄C peak is generated at 35.7°, which means that the in situ reaction has begun. Obvious TiB peaks and TiC peaks appeared in the sample as the temperature reaches to 950 °C, which means that a large number of reinforcing phases are formed in the composite material at this time. However, there is a (001)ₐₔ₁B₂ peak near 27.6°, indicating that the diffusion of Ti and B atoms during the solid-phase reaction is not sufficient. The possible side
reactions are as follows [18, 19]:

\[
\begin{align*}
\text{Ti} + 2\text{B} & \rightarrow \text{TiB}_2 \\
3\text{Ti} + \text{B}_4\text{C} & \rightarrow \text{TiB}_2 + \text{TiC} \\
\text{TiB} + \text{B} & \rightarrow \text{TiB}_2
\end{align*}
\]

No diffraction peak for B\(_4\)C and TiB\(_2\) is observed in all of the XRD spectra patterns for the composites sintered above 1050 °C, indicating that the \textit{in situ} reaction is nearly completed as the temperature reaches to 1050 °C.

### 3.2. Effect of sintering temperature on relative density, microstructure, and grain size

The relative density of composites sintered at different temperatures is shown in figure 2. It reveals that the density increases with the increase of sintering temperature and tends to be saturated above 1050 °C. The relative density of composite is very low at 550 °C and 650 °C, only 76.8% and 85.1%, respectively. When the sintering temperature is increased to 750 °C, the relative density of the composites increases to 94.5% rapidly.

Figures 3(a)–(g) shows the SEM images of composites sintered at various temperatures. It can be seen that obvious pores can be observed in the composite sintered at 550 °C, and only partial connections are formed between adjacent particles, indicating that the composite is less dense at this time. The contact surface between TC4 particles expands and the porosity decreases when the sintering temperature reached to 650 °C. The remaining pores in the matrix are mainly distributed at the interface formed by multiple TC4 particles and the B\(_4\)C phase enrichment area.

As the sintering temperature rises to 750 °C, the original characteristic surface of the powder particles disappears, and the matrix structure exists in the form of crystal grains. The dark gray area in the crystal grain is \(\alpha\)-Ti, and the bright color area is \(\beta\)-Ti. There are no obvious pores at the matrix grain interface and \(\alpha\)-Ti phase interface, indicating that the composites are further dense. Small white needlelike (TiB) and light gray round block (TiC) reinforcements appear in the matrix, while the number of B\(_4\)C particles decreases rapidly. It indicates that B\(_4\)C has participated in the reaction and is consumed at this temperature, which is also consistent with the previous XRD analysis results. In addition, it can be seen that there are obvious micro-gaps between the reaction product and the surrounding matrix. Figure 4(a and b) are the partial enlarged SEM image near the gaps, and the statistical result of the gap width respectively. As shown, the average gap width is 1.52 μm. The main reason for the formation of micro-voids is that the \textit{in situ} reaction products TiB and TiC have higher densities than the reaction raw material B\(_4\)C, so volume shrinkage occurs in areas where the reaction is violent. With the further increase of sintering temperature, the width of the micropores between the reaction products and the surrounding matrix gradually decreases and finally closes, which is accompanied by the increase of the relative density of the composite.

Figures 4(c)–(e) are high-magnification SEM images of TiB whiskers in composites sintered at 750 °C, 850 °C, and 950 °C, respectively. It is worth noting that there are many small particles on the surface of the \textit{in situ} formed TiB whiskers at 950 °C and below. These particles are equiaxed and mainly distributed on the whiskers.
near the reactants. The TEM image and corresponding SAED pattern of composite sintered at 750 °C is presented in figure S2. According to the results of EDS point scanning, as shown in table 1, the atomic ratio of Ti to B in the particles is close to 1:1.6. Due to the fact that boron atomic number is as low as 5, the number of B atoms excited by the secondary electron of the energy spectrometer will be slightly lower than the actual value. Combined with the XRD and TEM analysis results, it is inferred that the composition of small particles is TiB₂ phase. The separation of the ceramic primary phase and the matrix caused by the volume shrinkage at 750 °C and the rapid decrease in the atomic ratio of Ti to B in the reaction zone are the main reasons for the formation of small TiB₂ particles. Figure 4(f) shows the statistical results of the particle size of TiB₂ particles at various temperatures. It can be seen that between 750 °C and 950 °C, as the sintering temperature increases, the particle diameter continues to decrease, and the distribution density continues to decrease. When the sintering temperature is increased to 1050 °C and above, the TiB₂ particles on the surface of TiB whisker reacted completely and disappeared.

Figure 5 shows the particle (or grain) size of the matrix at different sintering temperatures. As shown, when the sintering temperature is 550 °C and 650 °C, the in situ reaction has not yet started, and most of the matrix particles are similar in size to the original TC4 powder, with an average particle size of 31.3 μm and 31.0 μm, respectively. When the sintering temperature reaches 750 °C, grain boundaries begin to form between the matrix particles, but they are consumed due to the reaction between the surface particles and B₄C. At this time, the grain size is smaller, about 28.3 μm. As the sintering temperature continues to rise, the grain growth is very slow. Grain growth is realized by grain boundary migration, which depends on the driving force of grain boundary diffusion ($P_\text{gr}$) and grain boundary curvature. For equiaxed grains, the curvature is related to the grain radius ($R_\alpha$). According to the theory of Kertsch L et al, the grain boundary migration rate is proportional to $P_\text{cr}$. However, the introduction of the second phase at the grain boundary will hinder the movement of the boundary, so the migration rate of the grain boundary can be expressed as [20, 21]

$$\frac{\dot{R}_\alpha}{M_{gb}} = \begin{cases} 0, & P_\alpha \leq P_\text{cr} \\ \frac{P_\alpha}{P_\alpha - \text{sign}(P_\alpha) P_\text{cr}}, & P_\alpha > P_\text{cr} \end{cases}$$

(4)

Where, $M_{gb}$ is the temperature-related migration coefficient and $P_\alpha$ is the critical diffusion driving force. According to the formula, when the diffusion driving force is lower than $P_\text{cr}$, the grain will not grow. Based on the classical Zener Drag pinning theory, $P_\alpha$ can be expressed as [22]:

$$P_\text{cr} = 1.5 \cdot \frac{f_\sigma}{r}$$

(3.6)
Where, $f$ is the fixed coefficient (0.93), $\sigma$ is the strength of the second phase, and $r$ is the particle size of the second phase. In this experiment, the size of dispersed TiC and TiB$_2$ particles near the whisker surface is small, which has a great hindrance to grain boundary migration. Therefore, the grain growth rate is slow when the sintering temperature is lower than 1050 °C. When the temperature increased to 1150 °C, the grain growth rate increased significantly. On the other hand, the increase of temperature provides more energy for grain boundary migration, which increases the driving force of grain boundary diffusion. On the other hand, with the increase of TiC particle size and the disappearance of TiB$_2$ particle reaction, $P_{cr}$ also decreased, and more grain boundaries were able to participate in the migration.

### 3.3. Mechanical properties

The tensile properties of composites sintered at different temperatures are shown in figure 6. The fracture surface images of the composites sintered at 850 °C, 950 °C, 1050 °C and 1150 °C are provided in figure S3. The composite sintered at 550 °C has no plasticity due to its low density and aggregation of particles only by external pressure. As a result, brittle fracture occurs in the testing process, and the obtained data are not reliable, so it is not shown in the figure. At the sintering temperature of 650 °C, the ultimate tensile strength of composite is only 92.1 MPa, and the effective yield strength and elongation cannot be obtained.

When the sintering temperature is higher than 750 °C, the relative density of the composite increases rapidly, so the performance index of each phase is stable. With the increase of sintering temperature, the tensile strength and yield strength of composites increase first and then decrease. In the range of 750 °C to 850 °C, the strength of composite increases the most. The reason is that the pores between reactants and products and matrix are closed, and the strength of phase interface is increased, so that TiB and TiC phases can fully play the role of load transfer and dislocation strengthening [23].

When the sintering temperature is 1050 °C, the composites have the highest tensile strength (1129.0 MPa) and yield strength (1077.8 MPa). When the sintering temperature is 1150 °C, the strength of the composite decreases. The results are mainly related to three factors: (1) the coarsening of TiB whiskers at 1150 °C and the formation of a large number of interface defects increase the number of crack sources on the surface of TiB whiskers, and it is easy to fracture in advance; (2) The matrix grain grows with increasing temperature. According to Halle-Petch theory, the strength of materials is inversely proportional to the square root of grain size [24]. (3) The degree of TiB reunion increased.

Moreover, it can also be analyzed that the elongation of composites increases with the increase of sintering temperature in the range of 750 °C to 1050 °C. Although the in situ reaction has started at 750 °C, the dislocation caused by the coordinated deformation in the grain cannot slip to the adjacent grain because the contact surface of the adjacent matrix becomes smaller due to the micropores, resulting in extremely low plasticity of the material (0.9%). When the temperature is 850 °C, the pores at the grain interface decrease and the number of effective grain boundaries increases, so that multiple grains can cooperate to deform, so the elongation of the material increases rapidly to 3.3%.

As the sintering temperature continues to rise to 950 °C, the particle size of the matrix is stable, and the composite becomes denser. In previous studies, the plasticity of composites can be significantly improved by increasing the whisker aspect ratio and relative density [25, 26]. However, the experimental results show that the plasticity change of the composites is very small at this stage. The main reasons are as follows: (1) The influence of TiB$_2$ particles. At this temperature, TiB whisker surface is covered with TiB$_2$ particles. Although common

![Figure 6. Room-temperature tensile properties of composites sintered at different temperatures.](image-url)
lattice interfaces can be formed between TiB, TiB₂ and matrix, the interfaces between TiB and TiB₂ are poorly matched. Therefore, cracks tend to occur near the whisker surface during the deformation process, which leads to premature fracture and reduced plasticity of the material.

The solution of carbon will strengthen the matrix and reduce the plasticity. When the sintering temperature is 1050 °C, the elongation of the material suddenly increased to the highest value of 7.1%, and the fracture form changed from brittle fracture to ductile fracture.

4. Discussion

4.1. Mechanisms of in situ reaction and reinforcements growth
According to the microstructure evolution of the composites (figures 3 and 4), the in situ reaction process inside the composites can be divided into four stages: primary phase formation stage, volume shrinkage side reaction stage, full reaction stage and enhancement phase growth stage. The specific reaction process is shown in figure 7.

In order to accurately analyze the morphology evolution of in situ TiB whisker and TiC particles, the diameter, aspect ratio of TiB and particle size of TiC in composites sintered at 750 °C to 1150 °C were calculated. The statistical results are shown in figure 8.

It can be inferred that sintering temperature has a great influence on TiB morphology, mainly in two aspects.

(1) The primary phase diameter of TiB is very small, only about 60 nm at 750 °C. With the increase of sintering temperature, whisker coarsening occurs twice. The first stage of coarsening occurs at 850 °C to 950 °C, and...
the average whisker diameter increases to 0.17 μm. At this stage, a large number of small boron-rich particles are attached to the surface of the generated whisker, resulting in a decrease in the concentration of B atoms at the whisker growth front, thus inhibiting the normal growth of TiB whisker along the direction [010]. However, with the increase of temperature, the substrate phase and boron-rich particles become more reactive, and nucleate and grow on the surface of attached TiB whisker in a certain direction, resulting in the coarsening of the original whisker.

The second stage of coarsening occurs at 1050 °C and above, during which the whisker coarsening rate is higher than that of the first stage. At 1150 °C, the average whisker diameter suddenly increases to 0.46 μm. According to figure 3g, there are two ways of whisker coarsening: (I) Single whisker grows along radial direction. (II) Adjacent whiskers growing in the same direction can form a certain orientation interface between the side surfaces parallel to the growth direction. With the growth and expansion of the interface, multiple adjacent whiskers can fuse into a thicker whisker, resulting in a large increase in the average whisker diameter.

(2) The average length of TiB whiskers between 750 °C and 1050 °C is 0.52 μm, 1.63 μm, 5.05 μm and 6.31 μm, respectively. The volume shrinkage caused by in situ reaction at 750 °C results in partial separation of the reactants from the matrix, so the whisker growth is slow at this stage. At 850 °C, the whisker grows at the highest rate along the length direction due to the closure of interfacial pores and re-contact of reactants with titanium matrix. With the increase of sintering temperature, the growth rate of whisker slows down and becomes saturated at 1050 °C.

The slenderness ratio of TiB whisker increases first and then decreases with the increase of sintering temperature. When the sintering temperature is lower than 1050 °C, the slenderness ratio increases almost linearly with an average increase rate of 0.082 / °C. At 1050 °C, the TiB whisker length–diameter ratio reached the highest value of 33.2. When the temperature is higher than 1050 °C, the aspect ratio decreases greatly and is only 12.0 at 1150 °C.

In addition, compared with (TiB + TiC)/TMCs prepared by traditional methods [27, 28], the TiB slenderness ratio of composites prepared by SPS is higher at the same sintering temperature, for two reasons: (I) In SPS sintering process, the activity of Ti and B atoms in the reactants is increased, and the migration mode is not limited to the diffusion of atoms along grain boundaries, but also can be dispersed by melting/evaporation-condensation mode, thus accelerating the growth of TiB whiskers along the axial direction. (II) The SPS generates heat in the sample and in adjacent molds through a dense current, so precise control of the sintering body temperature can be achieved by adjusting the current density. In addition, due to the low temperature of the furnace chamber, the temperature of the sintered body is very sensitive to the current intensity. After the whisker grows to the best shape, the current can be reduced immediately to cool down, thus avoiding the excessive growth of whisker.

Furthermore, TiC particles are mainly equiaxied in the matrix, and their particle diameters are distributed in a wide range at various sintering temperatures. The average particle size increases with the increase of sintering temperature. At the sintering temperature of 750 °C, the average diameter of the primary TiC phase is 0.15 μm, and the particle size distribution ranges from 0.11 μm to 0.23 μm. With the increase of sintering temperature, TiC growth occurs only once in the range of 850 °C to 950 °C. At this stage, the average growth rate of particles is 3.3 nm / °C, which is mainly due to the reactant recontact with matrix, which accelerates the mutual diffusion between Ti and C. In the remaining temperature range, TiC growth rate is relatively stable, the average growth rate is about 1.0 nm / °C. The maximum mean particle size of TiC is 0.8 μm, which reaches at 1150 °C, and the particle size distribution ranges from 0.37 μm to 1.8 μm. In addition, combined with SEM images, it can be
found that above 850 °C, some TiC appear elliptic, and a small number of particles appear wavy shape on the surface. These morphological changes indicate that TiC particles will also undergo deformation at this temperature. Its deformation is related to the initiation of TiC slip system at temperatures above 800 °C [111] <110> and {001} <110> [29, 30].

4.2. Densification mechanism

Figure 9 shows the temperature, pressure and absolute displacement curves of composite in SPS process with time at 1150 °C. As can be seen from the figure, the absolute displacement of the sample decreases gradually with the increasing of temperature from room temperature, indicating that the composite expands during heating. At 354 °C to 410 °C, the sample expands obviously, which is caused by the evaporation of water vapor and ethanol absorbed by powder particles. The sintering pressure in this temperature section is very low, only 1 MPa, so the gas generated in the sample cannot be completely discharged in a short time, but can be distributed in the gap between particles, and its pressure value increases with the increase of temperature.

As the sintering temperature continues to increase, the sample stops expanding, but the measured pressure fluctuates and decreases slowly. The measured pressure value at the sample is the sum of the applied mechanical pressure value and the thermal stress value generated by the expansion in the sample. Since the applied mechanical force is constant 0.7 kN, and the metal TC4 powder expands continuously with the temperature rise, the thermal stress generated should also increase continuously. Therefore, pressure reduction at this stage can only be realized by gas discharge and pressure reduction at the intergranular spaces.

When the temperature rises to 656 °C, the displacement increases gradually, indicating that the sintered body begins to shrink. At this point, the in situ reaction did not start. The contraction factor was that TC4 particles softened, connected with each other and deformed under the initial pressure. Subsequently, as the sintering temperature further increases, the sintered body continues to shrink, and the sintering force is loaded at a constant rate of 0.07 kN/s at about 1040 °C.

It can be found that the shrinkage process is not linear, which is mainly related to the stage of the in situ reaction process. The shrinkage law of the composite powder in each sintering stage can be further studied by the change rate of displacement and the change of resistance of the sintered body. Figure 10 shows the variation curves of displacement rate and resistance of composite with time in the process of SPS preparation. It can be seen that the rapid shrinkage of the composite has five peak values, which are 0.038 mm s⁻¹, 0.138 mm s⁻¹, 0.230 mm s⁻¹, 0.095 mm s⁻¹ and 0.178 mm s⁻¹ respectively. The corresponding peak temperatures are 663 °C, 758 °C, 840 °C, 994 °C and 1060 °C respectively. The corresponding measured loads were 1.3 kN, 0.4 kN, 0.5 kN, 1.2 kN and 3.7 kN, respectively.

In the initial stage of sintering (0 s to 153 s), the displacement of the punch is very small under the action of pre-pressurization. As the temperature increases, the displacement rate slowly increases and fluctuates, while the resistance drops rapidly from 4.42 × 10⁻³ Ω to 3.37 × 10⁻³ Ω. The actual resistance is divided into two parts: the intrinsic resistance of the powder and the contact resistance. During the shrinkage of the sintered body, the TC4 and B4C particles are in a chemically stable state, so the intrinsic resistance does not change, but the particle spacing continues to decrease, so the powder is reduced. Contact resistance in the body.

At 360 s, the first obvious peak value of 0.038 mm s⁻¹ appeared on the curve of displacement change rate, and the temperature was 663 °C at this time. At this stage, some of the gaps between the TC4 powder particles began to close. The current flowing through the powder produces a large amount of Joule heat, and at the same
time it discharges on the surface of the particles, so that high-density energy is stored on the surface and inside of the powder. In the process of energy release, there is a tendency for the particles to rearrange to expand the contact area, so that the shrinkage rate increases rapidly. In addition, the embedding of hard B₄C particles into the softened TC4 particles is also an important factor for rapid densification. It is worth noting that in this temperature range, the resistance of the composite increases temporarily. Combined with the SEM image of composite sintered at 650 °C, the embedding of hard B₄C destroyed part of the interface morphology between TC4 particles, and the conductivity of B₄C was much lower than that of TC4, which led to the increase of contact resistance between TC4 particles.

The second peak shrinkage of 0.138 mm s⁻¹ appears at 405 s, when the sintering temperature is 758 °C. At this stage, the reaction activity of B₄C particles increases, TiB and TiC nucleate on a large scale, and tiny primary phases have also formed. Moreover, the diffusion rate of atoms between the matrix grains also increases significantly with the increase of the sintering temperature, resulting in rapid shrinkage. At the same time, the electrical resistance of the sintered body gradually decreases as the sintering temperature increases.

At a sintering temperature of 840 °C, the third and highest shrinkage peak appeared in the sintering curve, with a peak value of 0.230 mm/s. Comparing the histograms at 750 °C and 850 °C, it can be seen that the interface pores generated by the volume shrinkage during the in situ reaction are closed at the temperature of 840 °C, thus increasing the shrinkage rate. The reduction of matrix interface defects and the formation and growth of TiB whiskers with excellent conductivity improve the conductivity of the composite, so the resistance is further reduced to 2.62 × 10⁻³ Ω.

The fourth peak shrinkage of 0.095 mm s⁻¹ was reached at 994 °C. At this stage, the sintering temperature is close to the phase transition point, and some areas have changed from α phase to β phase. The corresponding main deformation mechanism has changed from dislocation slipping mechanism to dislocation climbing mechanism. Therefore, the flow stress of the composite is greatly reduced and the shrinkage is intensified [31].

The last shrinkage peak value of 0.178 mm s⁻¹ corresponds to a sintering temperature of 1060 °C. At this stage, as the sintering pressure increases, the sintered body shrinks significantly, and the electrical resistance also drops significantly. It shows that the sintering pressure is also an important factor in the densification of composites. Under the action of the sintering pressure, the plastic deformation ability of the matrix grains is improved, and the migration and rearrangement of the reinforcing phase particles are also smoother. The sintered body fills up the remaining pores in the interior through the deformation and local extrusion of the contact area between the phases, which promotes the increase of the relative density of the composite.

In the holding stage, the sintering pressure is loaded to the highest value, the shrinkage stops therewith, and the resistance tends to stabilize. The stable resistance is 1.73 × 10⁻³Ω.

5. Conclusion

(TiB + TiC) reinforced TC4 matrix composites were in situ synthesized by SPS process. The effect of sintering temperature on microstructure, grain size, mechanical properties and densification process of the (TiB + TiC)/TC4 matrix composites were investigated. Following conclusions can be obtained.

1. Below 1050 °C, the aspect ratio of TiB whiskers in the composite increases almost linearly, with an average increase rate of 0.082/°C. When the sintering temperature is 1050 °C, the aspect ratio reaches the highest value of 33.2. The diameter of TiB increases with the increase of sintering temperature, and rapid coarsening occurs twice in the temperature range of 850 °C – 950 °C and 1050 °C above.

2. The TiC grain size increases with the increase of sintering temperature, and rapid growth occurs only in the range of 850 °C to 950 °C. The average radial growth rate at this stage is 3.3 nm/°C. At other temperatures, the TiC growth rate is relatively stable. The average growth rate is 1.0 nm/°C.

3. With the increase of the sintering temperature, the tensile strength, yield strength and elongation of composites show a trend of first increasing and then decreasing. When the sintering temperature is 1050 °C, the composite has the highest tensile strength (1129.0 MPa), yield strength (1077.8 MPa) and plasticity (7.1%).

4. Before applying sintering pressure, the composite sintered body appears four shrinkage stages. The corresponding peak temperatures are 663 °C, 758 °C, 840 °C and 994 °C, respectively. The electrical resistance of sintered body decreases gradually with the increase of sintering temperature, and tends to be stable in the holding stage (1.73 × 10⁻³Ω), except for abnormal increase at 663 °C.
Acknowledgments

The authors acknowledge Dr Hao Wang and Dr Xian-Yu Li for their fruitful discussions and suggestions during the preparation of this manuscript.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Disclosure statement

No potential conflict of interest was reported by the authors.

ORCID iDs

Zheng-Yang Hu @ https://orcid.org/0000-0003-0181-0083
Zhao-Hui Zhang @ https://orcid.org/0000-0002-6021-1235

References

[1] Jiao Y, Huang L and Geng L 2018 Progress on discontinuously reinforced titanium matrix composites J. Alloys Compd. 767 1196–215
[2] Huang L, Geng L and Peng H 2015 Microstructurally inhomogeneous composites: is a homogeneous reinforcement distribution optimal? Prog. Mater. Sci. 71 93–168
[3] Hayat M D, Singh H, He Z and Cao P 2019 Titanium metal matrix composites: an overview Composites Part A: Applied Science and Manufacturing 121 418–38
[4] Li S, Sun B, Imai H, Mimoto T and Kondoh K 2013 Powder metallurgy titanium metal matrix composites reinforced with carbon nanotubes and graphite Composites Part A: Applied Science and Manufacturing 48 57–66
[5] Attar H, Ehtemam-Haghighi S, Kent D and Dargash M S 2018 Recent developments and opportunities in additive manufacturing of titanium-based matrix composites: a review Int. J. Mach. Tools Manuf 133 85–102
[6] Banerjee D and Williams J C 2013 Perspectives on titanium science and technology Acta Mater. 61 844–79
[7] Huang L, Geng L, Li A B, Yang F Y and Peng H X 2009 In situ TiBw/Ti–6Al–4V composites with novel reinforcement architecture fabricated by reaction hot pressing Scr. Mater. 60 996–9
[8] Huang L, Geng L, Fu Y, Kaveedran B and Peng H X 2013 Oxidation behavior of in situ TiCp/Ti6Al4V composite with self-assembled network microstructure fabricated by reaction hot pressing Corros. Sci. 69 175–80
[9] Hu Z Y, Cheng X W, Li S L, Zhang H M, Wang H, Zhang Z H and Wang F C 2017 Investigation on the microstructure, room and high temperature mechanical behaviors and strengthening mechanisms of the (TiB + TiC)/TC4 composites J. Alloys Compd. 726 240–53
[10] Mohammadzadeh A, Azadbeh M, Danningher H and Namini A S 2020 Ti–TiB2 composites consolidated by spark plasma sintering: Reaction mechanism, characteristics of in situ formed phases and densification behavior Mater. Chem. Phys. 242 122356
[11] Huang L, Geng L, Fu Y, Kaveedran B and Peng H X 2013 Oxidation behavior of in situ TiCp/Ti6Al4V composite with self-assembled network microstructure fabricated by reaction hot pressing Scr. Mater. 60 996–9
[12] Singh N, Ummethala R, Karamched P S, Sokkalingam G and Prashanth K G 2021 Spark plasma sintering of Ti6Al4V metal matrix composites: Microstructure, mechanical and corrosion properties J. Alloys Compd. 865 158875
[13] Ozerov M, Klimova M, Kolesnikov A, Stepanov N and Zherebtsov S 2016 Deformation behavior and microstructure evolution of a Ti/TiB metal–matrix composite during high-temperature compressive tests Mater. Des. 122 17–26
[14] Shen X, Zhang Z, Wei S, Wang F and Lee S 2011 Microstructures and mechanical properties of the in situ TiB–Ti metal–matrix composites synthesized by spark plasma sintering process J. Alloys Compd. 509 7692–6
[15] Hu Z Y, Zhang Z H, Cheng X W, Wang F C, Zhang Y F and Li S L 2020 A review of multi-physical fields induced phenomena and effects in spark plasma sintering: Fundamentals and applications Mater. Des. 191 108662
[16] Zhang Z, Liu Z, Lu J, Shen X, Wang F and Wang Y 2014 The sintering mechanism in spark plasma sintering—proof of the occurrence of spark discharge Scr. Mater. 81 56–9
[17] Song B, Kenel C and Dunand D C 2020 3D ink–extrusion printing and sintering of Ti, Ti–TiB and Ti–TiC microlattices Additive Manufacturing 35 101412
[18] Chaudhari R and Bauri R 2018 A novel functionally gradient Ti/TiB/TiC hybrid composite with wear resistant surface layer Acta Mater. 112 17–26
[19] Rahoma H K S, Wang X P, Kong F T, Chen Y Y, Han J C and Derradji M 2015 Effect of (α+β) heat treatment on microstructure and mechanical properties of (TiB + TiC)/Ti–B20 matrix composite Mater. Des. 87 488–94
[20] Kertsch L and Helm D 2016 Modelling grain growth in the framework of Rational Extended Thermodynamics Model. Simul. Mater. Sci. Eng. 24 045001
[21] Kertsch L and Helm D 2018 A thermodynamically consistent model for elastoplasticity, recovery, recrystallization and grain coarsening Int. J. Solids Struct. 152 183 185–95
[22] Vanherpe L et al 2010 Pinning effect of spheroid second–phase particles on grain growth studied by three–dimensional phase–field simulations Comput. Mater. Sci. 49 340–30
[23] Zhang X et al 1999 In situ technique for synthesising (TiB + TiC)/Ti composites Scr. Mater. 41 39–46
[24] Hill D et al 2005 Formation of equiaxed alpha in TiB reinforced Ti alloy composites Scr. Mater. 52 387–92
[25] Huang L, Qian M, Liu Z, Nguyen V T, Yang L, Wang L and Zou J 2018 In situ preparation of TiB nanowires for high-performance Ti metal matrix nanocomposites J. Alloys Compd. 735 2640–5
[26] Li H, Jia D, Yang Z and Zhou Y 2020 Achieving near equiaxed α-Ti grains and significantly improved plasticity via heat treatment of TiB reinforced titanium matrix composite manufactured by selective laser melting J. Alloys Compd. 836 155344

[27] Wei S L et al 2018 Interactive effects of cyclic oxidation and structural evolution for Ti–6Al–4V/(TiC + TiB) alloy composites at elevated temperatures J. Alloys Compd. 752 164–78

[28] Ivasishin O M et al 2019 Multi-layered structures of Ti–6Al–4V alloy and TiC and TiB composites on its base fabricated using blended elemental powder metallurgy J. Mater. Process. Technol. 269 172–81

[29] Lei C, Du Y, Zhu M, Huo W, Wu H and Zhang Y 2021 Microstructure and mechanical properties of in situ TiC/Ti composites with a laminated structure synthesized by spark plasma sintering Mater. Sci. Eng. A 812 141136

[30] Cao L, Wang H W, Zou C M and Wei Z J 2009 Microstructural characterization and micromechanical properties of dual-phase carbide in arc-melted titanium aluminide base alloy with carbon addition J. Alloys Compd. 484 816–21

[31] Kumari S et al 2004 High-temperature deformation behavior of Ti–TiBw in–situ metal–matrix composites Journal of the Minerals Metals and Materials Society 56 51–5