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Densification and microstructural studies of titanium–boron carbide (B_4C) powder mixture during spark plasma sintering

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ABSTRACT

The present study investigates the densification behavior of Ti–B_4C powder mixture based on the analysis of linear shrinkage and current data obtained during spark plasma sintering. Pure titanium attains faster densification than Ti–B_4C powder mixture. Ti–B_4C powder mixture takes higher temperatures to achieve maximum densification as B_4C percentage increases. The phase evolution of TiB and TiC according to the in-situ reactions was analyzed by X-ray diffraction (XRD) technique. Scanning electron microscopy (SEM) images provide evidence that the massive spherical particles transform into equiaxed and needle like structures over increasing sintering time. Energy dispersive spectroscopy (EDS) analysis reveals the presence of TiB and TiC reinforcements as needle like and equiaxed structures respectively.

1. Introduction

Among several in-situ ceramic particles or whiskers reinforced Titanium Matrix Composites (TMCs), Ti/(TiB + TiC) composites have generated considerable research interest over recent years. TiB and TiC particulates are preferred reinforcements due to their excellent thermodynamic stability, strong interfacial bonding and similar thermal expansion co-efficient with titanium matrix [1]. TiB and TiC also possess some desirable mechanical and electrical properties such as high hardness, low density, good corrosion resistance and excellent electrical conductivity [2–4]. Recent years of research have yielded results to suggest that the morphology of TiB and TiC can significantly affect the mechanical properties of Ti/(TiB + TiC) composites. During tensile loading, TiB whiskers can undertake more load than TiC. However, TiC spherical particles prevent crack nucleation and crack propagation is restricted more effectively than TiB [5]. Due to their unique microstructural evolution, the incorporation of TiB and TiC reinforcements is expected to improve the mechanical and tribological properties of titanium and its alloys. TMCs are commonly fabricated by P/M method because of its ease of fabrication and simple processing technique. Also, P/M method facilitates near net shape formability and offers the fabricator a good control over determining the final properties of the TMCs. However, conventional P/M processing methods of TMCs have their own limitations in the form of residual micro-porosity, uneven distribution of reinforcements and control of matrix reinforcement interface [6]. To overcome these limitations, advanced processing methods like in-situ processing techniques have been developed to fabricate TMCs. In-situ processing techniques have several advantages over conventional processing techniques such as good thermodynamic stability of reinforcements, uniform distribution of reinforcements, clean and improved matrix reinforcements interface [7,8]. Spark plasma sintering has emerged as an efficient sintering technique to consolidate the powders to achieve density almost equal to theoretical density [9]. This paper investigates the densification behavior and microstructural evolution of Ti/B_4C powder mixture by spark plasma sintering. Densification behavior is expected to be a function of linear shrinkage which in turn depends on the sintering temperature, pressure, time and current intensity. However,

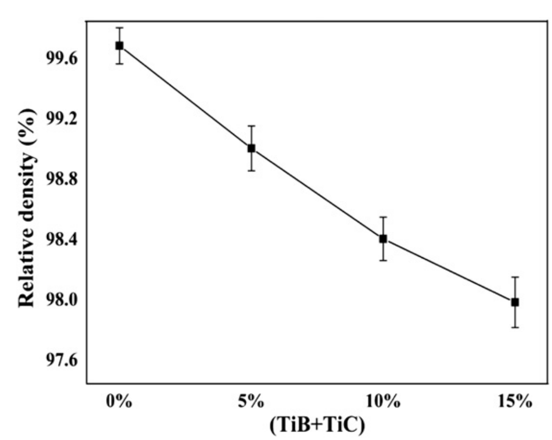

Fig. 1. Relative density of titanium and Ti/(TiB + TiC) composites sintered at 30 min.

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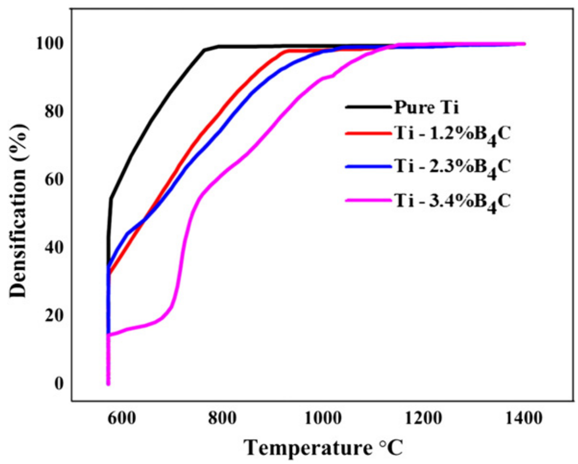

Fig. 2. Densification curves of titanium and Ti/B_4C powder mixture sintered at 30 min.

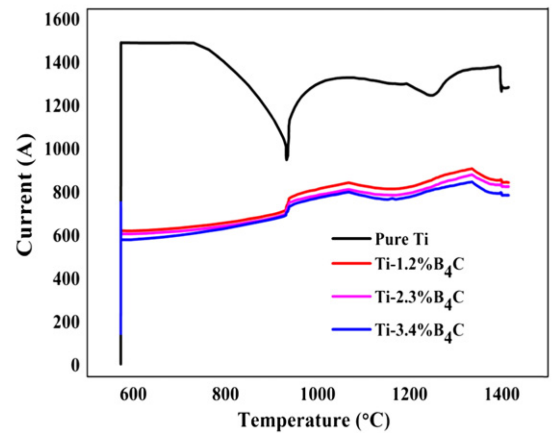

Fig. 3. Current curves of titanium and Ti/B_4C powder mixture sintered at 30 min.

in SPS method, sintering temperature and current intensity are significant variables that help to understand the densification behavior [10, 11]. Therefore understanding the individual effects of sintering parameters such as sintering temperature, time and current density on the densification behavior and the final microstructure of Ti/B_4C powder mixture is important.

2. Experimental work

The raw materials used for fabricating the Ti/(TiB + TiC) in-situ composite are primarily commercially pure titanium powder (Purity: 99.6%) and B_4C powder (Purity of 99%). The average particle size of Ti and B_4C powders was 100 μm and 50 μm, respectively. Three different weight fractions of B_4C powder were thoroughly mixed with titanium powder using centrifugal ball mill for 10 h. The powders were sintered at 1400 °C by Dr. SINTER SPS equipment, SPS SYNTEX, JAPAN with a heating rate of 150 °C/min up to 600 °C followed by 100 °C/min up to 1200 °C and then 50 °C/min up to 1400 °C. Sintering time was varied from 5 min to 30 min with constant pressure of 40 MPa. During the sintering process, the response of current and Z-axis movement were monitored. Bulk density of the sintered samples was measured by Archimedes principle. X-ray diffraction analysis was done with a scan rate of 0.02°/4 s using Rigagu ultima III, Japan with Cu-Kα radiation to study the phase evolution of TiB and TiC during sintering. Phase quantification analysis was done from the XRD patterns with the help of X'pert HighScore Plus. SEM studies were done to understand the in-situ phase evolution and morphological changes with respect to sintering time. EDS analysis was also done to confirm the chemistry of the particulates evolved during sintering.

Table 1
Temperature range, densification and densification rate.

Composition	Temperature range	Densification (%)	Densification rate (%/min)
Ti	Up to 573 °C	45	11
	573 °C to 850 °C	53	24
	850 °C to 1400 °C	2	<0.5
Ti–1.2%B_4C	Up to 573 °C	37	9
	573 °C to 900 °C	62	18
	900 °C to 1400 °C	1	<0.5
Ti–2.3%B_4C	Up to 573 °C	35	9
	573 °C to 950 °C	64	17
	950 °C to 1400 °C	1	<0.5
Ti–3.4%B_4C	Up to 573 °C	29	7
	573 °C to 1150 °C	70	15
	1150 °C to 1400 °C	1	<0.5

3. Results and discussion

3.1. Densification behavior

Fig. 1 shows the relative density values of Ti and Ti/(TiB + TiC) composites sintered at 1400 °C with a sintering time of 30 min. The relative density of pure titanium is found to be close to the theoretical density i.e. 99.74 ± 0.234%. However, it was observed that there is a slight decrease in the relative density of composites with increasing B_4C percentage. This is due to the presence of refractory phase B_4C and its reaction with titanium, which hinders the diffusion process leading to a decrease in the final relative density during sintering [12]. The measured relative density of Ti–5%(TiB + TiC), Ti–10%(TiB + TiC) and Ti–15%(TiB + TiC) composites is 99.06 ± 0.224%, 98.46 ± 0.223%, and 98.04 ± 0.236% respectively. Fig. 2 shows the densification curves of pure Ti and Ti/B_4C powder mixture sintered at 1400 °C for 30 min. Densification of pure Ti and Ti/B_4C powder mixture takes place in several stages at different densification rates. During the initial stages of sintering, pure Ti shows a significant increase in densification than Ti/B_4C powder mixture. Pure titanium was found to attain 45% densification at 573 °C. Spark discharge and particle sliding to the close-packed arrangement take place during the initial stages of sintering [13–16]. Spark discharge between the particles removes the surface oxide because of the voltage break down effect followed by the initiation of neck formation of powder particles [17]. It is noted that, pure titanium reaches 98% densification at a temperature of 850 °C. During this intermediate stage, densification is accelerated and rapid densification takes place due to the grain boundary diffusion leading into a complete neck formation between the particles [18]. However, after 850 °C, densification of pure titanium decreases and it reaches almost negligible percentage. Ti–1.2%B_4C and Ti–2.3%B_4C powder mixtures show 37% and 35% densification at 573 °C. Ti–1.2%B_4C takes 900 °C to achieve 99% densification and for Ti–2.3%B_4C, it takes 950 °C to achieve 99% densification. Ti–3.4%B_4C powder mixture shows 29% densification at 573 °C and the densification slowly accelerates and reaches 99% densification at 1150 °C. It is observed that the initial densification decreases with an increasing B_4C percentage. Consequently, it takes higher temperatures 850 °C, 900 °C, 950 °C and 1150 °C to achieve full densification for Ti, Ti–1.2%B_4C, Ti–2.3%B_4C and Ti–3.4%B_4C powder mixtures respectively. During the final stages of

Table 2
Quantitative analysis of Ti/(TiB + TiC) composites sintered at 30 min.

Composite	TiB (wt %)	TiC (wt %)	Ti (wt %)
Ti–5%(TiB + TiC)	3.40	2.61	Balance
Ti–10%(TiB + TiC)	6.57	5.97	Balance
Ti–15%(TiB + TiC)	10.18	6.54	Balance