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**FORMATION OF EQUIAXED ALPHA AND TITANIUM  
NITRIDE PRECIPITATES IN SPARK PLASMA SINTERED  
TiB/Ti-6Al-4V COMPOSITES (PREPRINT)**

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# Formation of equiaxed alpha and titanium nitride precipitates in spark plasma sintered TiB/Ti-6Al-4V composites

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## Abstract

Spark plasma sintered TiB/Ti-6Al-4V composites have been characterized using scanning electron microscopy (SEM), electron backscattered diffraction (EBSD) and transmission electron microscopy (TEM). As-SPS processed composites exhibit a more refined distribution of equiaxed  $\alpha$  precipitates as compared to arc-melted composites containing similar volume fraction of TiB precipitates. Additionally, SPS processed composites also show a highly refined distribution of TiN precipitates, as revealed by TEM studies.

**Keywords:** Ti-6Al-4V; TiB; TiN; Spark Plasma Sintering; Composite;  $\alpha/\beta$  phase

## Introduction

Trace amounts of boron addition to conventional titanium alloys has been found to have a considerable impact on the microstructure and the properties [1]. These composites offer improved mechanical properties by combining high strength and stiffness of TiB with the toughness of the Ti alloy matrix [2]. Several researchers have reported that addition of boron also results in refinement of prior  $\beta$  grain size as well as reduction in the  $\alpha$  grain size as TiB acts as pinning sites hence restricting grain growth [3-5]. Traditionally, powder metallurgy and common casting techniques were used to fabricate titanium matrix composites. In recent years, novel in situ processing techniques like spark plasma sintering (SPS), self-propagating high temperature synthesis (SHS) and laser engineered net shaping (LENS<sup>TM</sup>) etc. have aroused interest as they offer the advantage of a homogenous distribution of borides in the matrix [6]. Commercially used  $\alpha/\beta$  titanium alloys typically are subjected to thermo-mechanical processing to attain the desired microstructure relevant to the application. TiB precipitates have been found to influence the nucleation of  $\alpha$  phase by acting as heterogeneous nucleation sites in addition to the usual prior  $\beta$  grain boundaries. It has also been reported in the literature that  $\alpha$  nucleating from the TiB obeys an orientation relationship  $(001)_{\text{TiB}}// (0001)_{\alpha}$ ,  $[010]_{\text{TiB}}// [11-20]_{\alpha}$  [7]. The present paper discusses the effect of boron addition on the size and morphology of  $\alpha$  in TiB/Ti-6Al-4V composites fabricated using the SPS process and compares it with conventional arc-melted samples.

## Experimental

TiB<sub>2</sub> powder with a mean particle size of ~3 $\mu$ m was mixed with pre- alloyed Ti-6Al-4V powder of mean particle size ~30 $\mu$ m. Additional Ti powder was added to allow for reaction with TiB<sub>2</sub> to form TiB in order to maintain the composition of the base alloy. Mechanical alloying was carried out using planetary ball milling under nitrogen atmosphere and subsequently the powders were spark plasma sintered at a temperature of 1373K for 5 minutes employing a pressure of 50MPa under a vacuum of 10<sup>-3</sup>torr. For comparison purposes, Ti-6Al-4V/TiB composites with different volume fractions of TiB were also fabricated via arc-melting of pre-alloyed Ti-6Al-4V and TiB<sub>2</sub> powders. These arc-melted samples were solutionized at 1373K for 30 minutes followed by furnace cooling to allow for complete dissolution of  $\alpha$  during the  $\beta$  solutionizing process. The specimens were cut by wire electro discharge machining (EDM) and subsequently mechanically polished to a mirror finish using 0.05 $\mu$ m colloidal silica to minimize surface deformation. The microstructure was investigated using a FEI NOVA Nano SEM instrument. Electron backscatter diffraction (EBSD) studies were also carried out to determine the presence of orientation relationships between TiB and  $\alpha$  phase, if any. TEM investigations were carried out on conventional 3mm diameter disc samples. The TEM samples were analyzed in a FEI Tecnai F20 microscope operating at 200kV.

## Results and discussion

The overall microstructure of the SPS processed TiB/Ti-6Al-4V composite is shown in the backscatter SEM images, Figs. 1(a) and (b). The microstructure consists of acicular, needle-like TiB precipitates (dark contrast) dispersed in an  $\alpha$ + $\beta$  matrix with  $\alpha$  displaying an equiaxed (or globular) morphology. The higher magnification image in Fig. 1(b) shows the presence of an additional unknown fine scale spherical precipitate, homogenously distributed in the matrix. The TiB precipitates have an acicular morphology with a length of about 5-10 $\mu$ m and widths ranging from 0.5-2 $\mu$ m. The size range of the second reinforcement phase, exhibiting a spherical morphology, is 100-300nm. The area fraction of the borides was determined using basic two-dimensional image analysis techniques and was found to be ~1% and for simplicity this value was assumed to be an approximate measure of the boride volume fraction. This sample will henceforth be referred to Ti64-1TiB. Similar nomenclature will be adopted for other samples as well. Fig. 1(c) and (d) show the microstructure of the arc melted composites. The area fraction of the borides was found to be 1% and 2% respectively. The backscatter SEM images clearly show that the distribution of borides in the SPS processed Ti64-1TiB composite is more homogenous compared to the arc-melted composites where TiB appears to be decorating the prior  $\beta$  grain boundaries. The absence of TiB along prior  $\beta$  grain boundaries in the SPS processed sample is definitely an advantage of this type of processing, obviating the deleterious effects of  $\beta$  grain boundaries decorated by hard non-deformable TiB precipitates. The microstructural difference between the two processing routes arises from the fact that while arc-melting results in the entire system first melting and then solidifying, SPS process is primarily based on solid-state processing involving localized melting in some cases but does not involve homogeneous solidification of a liquid.

A common feature to be observed for all samples is that  $\alpha$  in the immediate vicinity of TiB appears to adopt an equiaxed morphology compared to  $\alpha$  further away from TiB precipitates which exhibits a more lath-like morphology. This effect is predominantly seen in case of the arc-melted Ti64-1TiB and Ti64-2TiB composites. These observations clearly indicate that the TiB precipitates influence the morphology of  $\alpha$  phase and consequently it is important to investigate the possible existence of orientation relationships between these two phases as discussed subsequently in this paper. The backscatter SEM micrographs clearly reveal that the Ti64-1TiB composite, processed by SPS, has much finer scale  $\alpha$  as compared to the arc-melted samples. The same level of refinement may be achieved by thermo-mechanical processing of the same microstructure in the  $\alpha+\beta$  regime but SPS offers the novel advantage that the refined equiaxed  $\alpha$  is obtained during sintering at a temperature above the  $\beta$  transus temperature. Therefore, SPS processing results in fine scale equiaxed  $\alpha$  formation in TiB/Ti-6Al-4V composites without the costs and time associated with an additional thermo-mechanical processing step post synthesis, as required for arc melted composites. From the SEM micrographs it is evident that SPS processing allows for a higher fraction of refined equiaxed  $\alpha$ , for much lower volume fractions of TiB, potentially leading to a superior balance of material properties as compared to composites with higher TiB volume fractions.

The results of crystallographic EBSD-orientation imaging microscopy (OIM) investigations of SPS processed Ti64-1TiB composite have been summarized in Fig. 2 with the inverse pole figure map of the overall microstructure shown in Fig. 2(a). Figs. 2(b) and (c) show specific selected TiB and  $\alpha$  precipitates, along with their corresponding pole figure maps. The pole figures clearly reveal two distinct orientation relationships between the TiB and  $\alpha$ , which are  $(001)_{\text{TiB}}//(\text{0001})_{\alpha}$ ,  $[010]_{\text{TiB}}//[11-20]_{\alpha}$  and  $(101)_{\text{TiB}}//(\text{01-10})_{\alpha}$ ,  $[010]_{\text{TiB}}//[11-20]_{\alpha}$  and will be subsequently referred to as OR1 and OR2 respectively. In recent studies on  $\beta$  titanium alloys the existence of multiple orientation relationships between  $\alpha$  and TiB have been reported [8, 9]. OR1 is the most commonly observed orientation relationship in TiB/Ti-6Al-4V composites but OR2 has not been reported for this system yet. Fig. 2(d) shows the inverse pole figure map from a different region of the SPS processed sample and a specific combination of a TiB and a  $\alpha$  precipitate together with their corresponding pole figures are shown in Fig. 2(e). The OR2 relationship between the TiB and the  $\alpha$  precipitate is evident in this case. Similar observations of ORs between TiB and  $\alpha$  in many different regions of the sample, clearly indicate that the TiB precipitates act as nucleation sites for  $\alpha$ . Based on these observations it can be speculated that the development of an orientation relationship between TiB and  $\alpha$  could potentially result in the loss of the classical Burgers orientation relationship between the  $\alpha$  precipitates and the  $\beta$  matrix. Consequently, the morphology of  $\alpha$  precipitates, that is closely associated with the  $\alpha/\beta$  orientation relationship, can change, leading to the formation of more equiaxed  $\alpha$  nucleating from the TiB.

Fig. 3(a) shows a bright field TEM image of the SPS processed Ti64-1TiB composite with a diffracting  $\beta$  pocket (dark contrast) between  $\alpha$  precipitates. Fig. 3(b) shows a TiB precipitate, with a high density of faulting within the boride aligned parallel to the  $(100)_{\text{TiB}}$  planes and Fig. 3(c) provides a clearer view of the high fault density within the boride and the electron diffraction pattern shown as an inset can be consistently indexed as the  $[001]$  zone axis of the orthorhombic B27 structure of TiB. The mechanism of

formation of facets in these TiB precipitates and faulting parallel to the the (100) planes, has been widely discussed in the literature [10, 11]. Fig. 3(d) shows a bright field TEM image of one of the unidentified precipitates in the SPS processed composite. Selected area diffraction analysis was carried out to determine the crystal structure of this unknown phase. These precipitates were found to have a face-centered cubic (*fcc*) crystal structure with a lattice parameter of  $a=0.42\text{nm}$ . Figs. 3(e) and (f) show converged beam micro-diffraction patterns of the unknown precipitate along the [001] and [113] zone axes respectively. EDS and EELS revealed the presence of nitrogen peaks in these precipitates hence they are likely to be TiN. This argument is augmented by the fact that since the powders were mechanically alloyed in nitrogen atmosphere prior to sintering; it is highly likely that Ti reacts with the residual nitrogen to form TiN. These homogeneously distributed TiN precipitates are likely to enhance the strength of this composite via precipitation hardening.

## Conclusions

Based on EBSD and TEM studies it can be concluded that spark plasma sintering is a novel processing technique to obtain TiB/Ti-6Al-4V composites with fine scale equiaxed  $\alpha$  with small boron additions unlike arc melting which requires much higher boride volume fraction to achieve the same degree of refining. TiB has been found to act as nucleation sites for  $\alpha$  as evident from the orientation relationships between the two phases. The orientation relationships between these two phases are  $(001)_{\text{TiB}}// (0001)_{\alpha}$ ,  $[010]_{\text{TiB}}// [11-20]_{\alpha}$  and  $(101)_{\text{TiB}}// (01-10)_{\alpha}$ ,  $[010]_{\text{TiB}}// [11-20]_{\alpha}$  where the latter orientation relationship has been reported for the first time for this system. Additionally, a highly refined and homogeneous distribution of TiN precipitates was also observed within the matrix, possibly resulting from the nitrogen gas involved during mechanical alloying process prior to sintering.

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Figure Caption

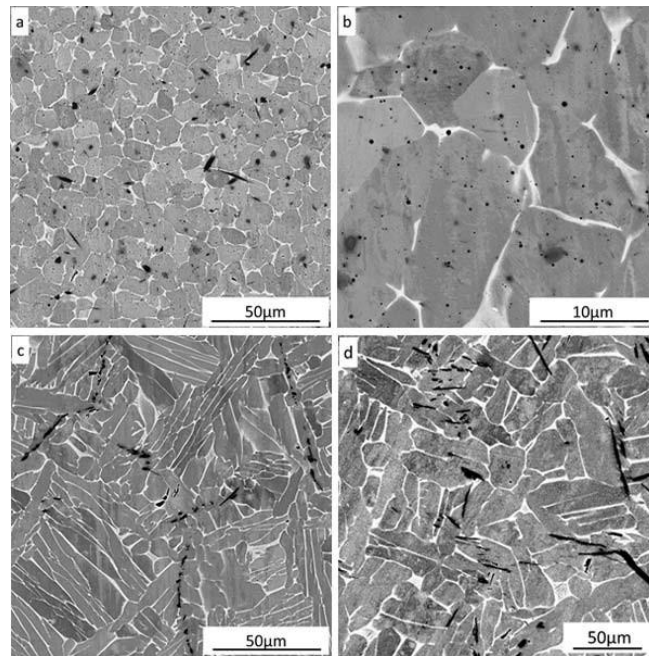


Fig. 1 Backscatter SEM images of SPS processed Ti64-1vol%TiB composite (a and b), arc melted Ti64-1vol%TiB composite (c) and arc-melted Ti64-2vol%TiB composite (d)

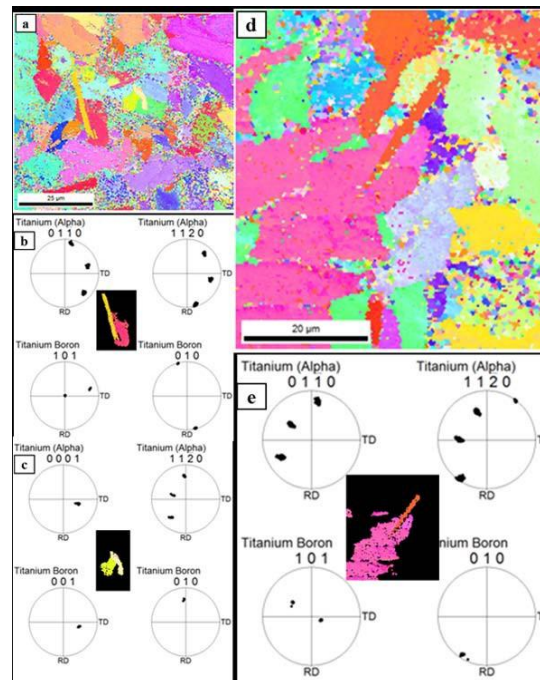


Fig. 2 (a) Inverse pole figure map of the overall microstructure of the SPS processed Ti64-1vol%TiB composite, (b) and (c) Highlighted regions consisting of selected boride precipitates and  $\alpha$  precipitates and their corresponding pole figures, (d) Inverse pole figure map of a different region of the SPS processed Ti64-1vol%TiB composite and (e) Selected TiB and  $\alpha$  precipitates with corresponding pole figures.

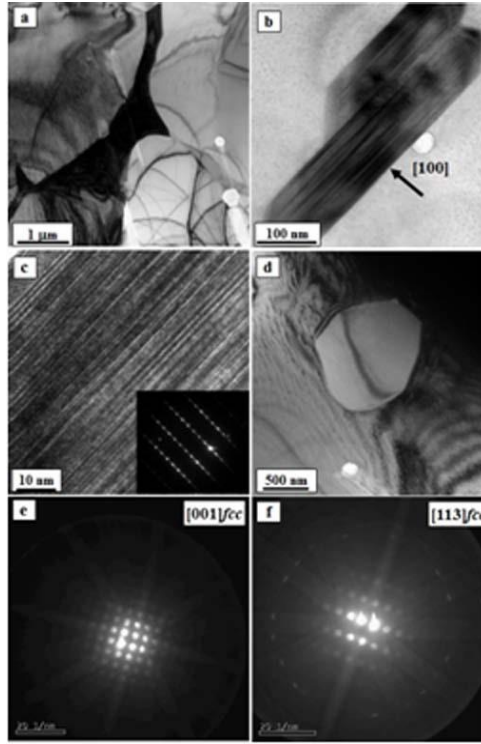


Fig. 3 (a) Bright field TEM image of the SPS processed 1.5 vol.%TiB/Ti-6Al-4V composite. (b) and (c) Higher magnification bright-field TEM images exhibiting a highly faulted TiB precipitate with faults parallel to  $(100)_{\text{TiB}}$  planes viewed along the  $[001]$  zone axis (diffraction pattern shown as an inset). (d) Bright field TEM image of an equiaxed precipitate of the second titanium nitride phase present in the matrix. (e) and (f) Converged beam micro-diffraction patterns which can be consistently indexed as the  $[001]$  and  $[113]$  zone axes of titanium nitride, respectively.