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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 α 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.

1. Introduction

Trace amounts of boron addition to conventional titanium alloys have 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 β grain size as well as reduction in the α 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™) etc. have aroused interest as they offer the advantage of a homogenous distribution of borides in the matrix [6]. Commercially used α/β 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 α phase by acting as heterogeneous nucleation sites in addition to the usual prior β grain boundaries. It has also been reported in the literature that α nucleating from the TiB obeys an orientation relationship $(001)_{TiB}//(0001)_{\alpha}$, $[010]_{TiB}//[11\text{–}20]_{\alpha}$ [7]. The present paper discusses the effect of boron addition on the size and morphology of α in TiB/Ti–6Al–4V composites fabricated using the SPS process and compares it with conventional arc-melted samples.

2. Experimental

TiB_2 powder with a mean particle size of ~3 μm was mixed with pre-alloyed Ti–6Al–4V powder of mean particle size ~30 μm. Additional Ti powder was added to allow for reaction with TiB_2 to form TiB in order to maintain the composition of the base alloy. Mechanical alloying was carried out using planetary ball mill (Planetary Mill, Fritsch GmbH) with a ball to powder ratio of 5:1 under nitrogen atmosphere for 18 h at 250 rpm and subsequently the powders were spark plasma sintered at a temperature of 1373 K for 5 min employing a pressure of 50 MPa under a vacuum of 10^{-3} 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_2 powders. These arc-melted samples were solutionized at 1373 K for 30 min followed by furnace cooling to allow for complete dissolution of α during the β solutionizing process. The specimens were cut by wire electro discharge machining (EDM) and subsequently mechanically polished to a mirror finish using 0.05 μm 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 α phase, if any. TEM investigations were carried out on conventional 3 mm diameter disc

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samples. The TEM samples were analyzed in a FEI Tecnai F20 microscope operating at 200 kV.

3. Results and discussion

The overall microstructure of the SPS processed TiB/Ti–6Al–4V composite is shown in the backscatter SEM images, Fig. 1(a) and (b). The microstructure consists of acicular, needle-like TiB precipitates (dark contrast) dispersed in an α+β matrix with α 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 μm and widths ranging from 0.5 to 2 μm. The size range of the second reinforcement phase, exhibiting a spherical morphology, is 100–300 nm. 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) shows the microstructure of the arc melted composites. The area fraction of the borides was found to be 1% and 10% 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 β grain boundaries. The absence of TiB along prior β grain boundaries in the SPS processed sample is definitely an advantage of this type of processing, obviating the deleterious effects of β grain boundaries decorated by hard non-deformable TiB precipitates. The formation mechanism of TiB in both the processes is governed by the following reaction

$$TiB_2 + Ti \rightarrow 2TiB.$$

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. During solidification of arc melted hypoeutectic compositions as discussed in this study, the primary solidification phase is β followed by nucleation of TiB at β grain boundaries as evident from the Ti–B binary phase diagram [8]. On the other hand, in SPS processing since there is no homogeneous solidification involved, a solid-state reaction between TiB_2 and Ti powders takes place, resulting in a more homogeneous distribution of TiB precipitates and the prior β grain boundaries remain virtually free of TiB.

A common feature to be observed for all samples is that α in the immediate vicinity of TiB appears to adopt an equiaxed morphology compared to α 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 Ti64–10TiB composites. As a result of a higher volume fraction of TiB in Ti64–10TiB, it can be noted, that there is a larger volume fraction of equiaxed α. These observations clearly indicate that the TiB precipitates influence the morphology of α 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 α 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 α+β regime but SPS offers the novel advantage that the refined equiaxed α is obtained during sintering at a temperature above the β transus temperature. Therefore, SPS processing results in fine scale equiaxed α 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 α, 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

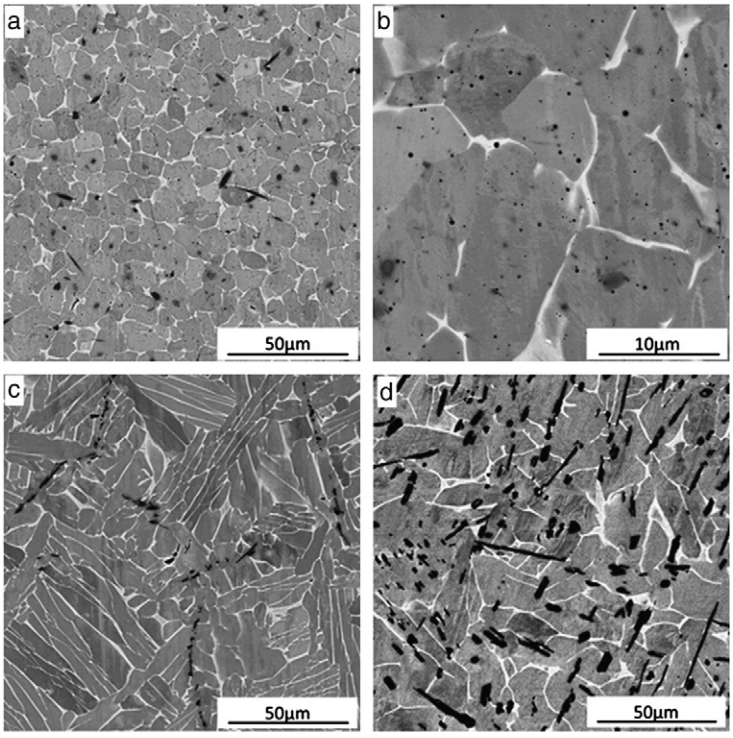

Fig. 1. Backscatter SEM images of SPS processed Ti64–1 vol%TiB composite (a and b), arc melted Ti64–1 vol%TiB composite (c) and arc-melted Ti64–2 vol%TiB composite (d).