Functionally Gradient Ti6Al4V-TiB Composite Produced by Spark Plasma Sintering

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Abstract. Functionally gradient materials (FGM) are progressive materials, where the final characteristics are sequentially changing with dimensions. Direct fabrication of functionally gradient Ti6Al4V-TiB composite was performed by spark plasma sintering (SPS) technique. Powder mixtures of six different ratios of Ti-alloy and TiB₂ were subjected to sintering at a temperature of 1350 °C and a pressure of 50 MPa with a dwelling time of 15 min to obtain a six-layer specimen. Scanning electron microscope images demonstrate smooth transition between layers. Vickers hardness (HV5) is 350 on the top side and 1038 on the bottom side, and a corresponding coefficient of friction (CoF) is 0.99 and 0.76, respectively, which demonstrates their different performance under sliding wear.

1. Introduction

The functionally gradient materials with heterogeneous (FGM) phase distribution throughout the volume possess the comprehensive properties of the constituent compounds gradually changing with dimensions. The coherent change in the content of an FGM component allows to overcome the interface disparity of different phases, provide the coherent coexistence and broaden the applicability of the material [1-4].

Titanium alloys (specifically Ti6Al4V) possessing light weight, high chemical stability, high strength and elastic modulus are capturing favored positions in aerospace, automotive and biomedical applications; however, their inferior tribological properties, mainly low wear resistance and a high coefficient of friction are suppressing the further conquer of new applications [5]. Thus, numerous compounds in powder or fiber form, have been reported to reinforce Ti, including carbides (WC, B₄C, TiC, SiC), borides (TiB₂, TiB), etc [6-8]. Adding TiB into Ti matrix is an advantageous approach to increase strength and the stiffness of the titanium matrix material (TMC), considering matching density and thermal expansion coefficients [8].

Spark plasma sintering (SPS) is a leading powder consolidation technology adopting the advantages of relatively low compaction temperatures, achieving full density of the materials, wide range of applied pressure and temperature, suppression of undesired grain growth and negligible material loss in comparison with conventional powder metallurgy techniques [9].

In this work, a set of functionally gradient Ti6Al4V-TiB composites was manufactured by spark plasma sintering using Ti6Al4V-TiB₂ powders mixtures. Hardness and sliding volume loss values were measured to confirm the different side performance of gradient sample; morphology were studied to show the gradient structure and component were analyzed to show the physico-chemical development during the consolidation process.
2. Experimental

2.1. Samples preparation

Commercially available Ti6Al4V (SLM Solutions, <63 µm) and TiB2 (Alfa Aesar, Thermo Fisher Scientific, <44 µm) powders were chosen as starting materials. Considering the large size of Ti6Al4V particles, the powder was initially sieved and the fraction with less than 20 µm was used for powder mixture preparation.

Six powders mixtures of Ti6Al4V-TiB2 with different weight ratio starting from pure Ti6Al4V to Ti6Al4V-TiB2 50-50 wt% with step size of 10 wt% TiB2 addition were prepared, corresponding to 100-0, 90-10, 80-20, 70-30, 60-40 and 50-50 wt% mixtures. For powder mixing the disintegrator DSL-175 with a combined inertial-centrifugal classifier was used in protective atmosphere (argon). The velocity of collision was set as 156 m·s⁻¹, thus, the specific energy of treatment was calculated as 18.4 kJ·kg⁻¹.

For gradient sample, powder mixtures with six different weight ratio of Ti6Al4V and TiB2 were layer by layer added to the graphite mold of 25.4 mm diameter, then consolidated using SPS device (FCT Systeme GmbH, Germany) in vacuum at temperature of 1350°C with simultaneous application of 50 MPa pressure for a dwell time of 15 min. The powder mixtures were heated up to sintering temperature with a heating rate of 100 °C·min⁻¹.

As a reference, individual powder mixtures with six different Ti6Al4V and TiB2 ratios were also prepared as independent samples using the same sintering parameters, as mentioned above. The preparation scheme of the independent and gradient samples are illustrated in Figure 1.

![Figure 1. Schematics of Ti6Al4V- (0-50 wt%) TiB2 independent samples and gradient sample preparation process](image)

2.2. Characterization

Sample section was polished and microstructural examination of the specimens was conducted using a Hitachi TM1000 scanning electron microscope (SEM). The Vickers hardness was estimated on the polished surface using Indentec 5030 SKV hardness tester applying a load of 49 N for 10 s. X-ray diffraction (XRD) data were collected using a Rigaku SmartLab SE diffractometer with a D/teX Ultra 250 1D detector. The measurements were performed at room temperature from 18 to 108° (2θ) with 0.01° step with 5 seconds per step.

2.3. Sliding wear test

A universal materials test device (UMT-2) supplied by CETR (Bruker) was engaged for materials testing under dry reciprocating sliding condition in ball-on-plate configuration. A ball of alumina with Ø3 mm
(Redhill Precision, Czech Republic), hardness HV10=1450 and roughness Ra=0.02 µm, was used as a counterbody. The frequency and amplitude of sliding was 5 Hz and 1 mm, respectively. The sliding load was 1N. The test consisted of 10 steps of 1000 sec each. The surface of the wear tracks evaluated by means of the 3D profilometer Bruker Contour GT-K0+ to determine the volume of material loss (net missing volume). Experiments were conducted in air at room temperature (20±2 °C) with a relative humidity (RH) of 45±5%.

3. Results and discussion

Figure 2 shows the SEM images of developed Ti6Al4V-(0-50 wt%) TiB₂ powders mixtures and respective produced samples. The sieved Ti6Al4V spherical shape powders with particle size <20 µm and TiB₂ powder of plate-like particles with mean size of 20 µm were homogeneously mixed by the disintegrator treatment. For the sintered gradient sample, each layer shows similar image as corresponding independent samples, and there was smooth transformation between each layer boundaries.

![Figure 2. SEM images of six disintegrator mixed Ti6Al4V-(0-50wt%) TiB₂ powders (first row), the sintered individual samples from each of these powder mixtures (second row), and different layers of the gradient sample (third row)](image)

Figure 3 shows the diffractograms of sintered independent samples and different regions of the gradient sample. The TiB phase formation occurs due to the reaction between Ti and TiB₂ following Ti+TiB₂→2TiB. The XRD patterns of independent samples demonstrate the gradual increase in TiB peak, when TiB₂ content in the initial mixture was increased, highlighting the intensive reaction between Ti and TiB₂ under the given conditions. Because of thin quasi-continuous layers of gradient sample, it was not possible to accurately divide all six regions, hence 4 regions were studied, as shown in Figure 3. Stepping from Region 1 to 4, a weakening of Ti peaks is visible in contrast to strengthened TiB peaks, as the Ti is consumed for TiB during reaction.

Figure 4 demonstrates the average volume loss (wear rate) and coefficient of friction (CoF) values of the materials tested. All the composites show low wear rates and CoF values in comparison to pure Ti6Al4V specimen, and a significant drop in wear rate with the increase in TiB₂ addition is noted. It is also revealed that the tribological behaviour of the bottom side of the gradient sample (produced from
Ti6Al4V-50%TiB₂ is closer to the independent sample produced from Ti6Al4V-40%TiB₂ mixture. The volume loss and CoF of the top surface of gradient sample (produced from pure Ti6Al4V) is more close to independent sample prepared from Ti6Al4V-10%TiB₂ mixture, than to the sample sintered from pure Ti6Al4V. Hence, during sintering the components of gradient sample diffused and tend to homogenize.

Figure 3. XRD patterns of six independent samples (sintered from Ti6Al4V- (0-50 wt%) TiB₂ mixtures) (left side) and XRD patterns of functionally gradient sample composing of altering quasi-continuous Ti-TiB composite layers (right side) along with reference Ti and TiB diffractograms

Figure 4. Average Volume loss and coefficient of friction for independent and gradient samples after sliding test
A higher wear rate for pure Ti6Al4V specimen is owed to its lower hardness and higher ductility. Severe ploughing, heavily deformed surface and abrasive cutting marks on the pure Ti6Al4V bulks during sliding is commonly reported as the reason behind poor tribological performance [10, 11, 12]. The intensification of wear of pure Ti6Al4V specimen is accompanied by its thermal softening due to frictional heating during sliding passes. A similar mechanism of wear in Ti6Al4V alloy was reported by others [11]. Development of surface cracks due to fatigue (cyclic) during reciprocating sliding is a practical phenomenon. Magaziner et. al reported a similar fatigue induced cracks on Ti6Al4V alloy in reciprocation sliding and termed it to be ‘fretting wear’ which in turn results in early crack initiation and its subsequent growth [12, 13].

A limited range of CoF fluctuation is noted for the composites prepared from mixtures containing 20-50 wt% of TiB2 addition. This is due to the possibility that the worn debris (or worn TiB particles) during sliding acted as third body and intensifies wear and CoF fluctuation. Generated third bodies are stated to induce localized stresses and accompanies the removal of soft matrix phase [13, 14]. Considering the measured hardness values (Vickers) of gradient sample are 350 HV5 for top surface and 1038 HV5 for bottom surface, which are similar to the corresponding individual samples (331 HV5 for sample prepared from pure Ti6Al4V and 1024 HV5 for sample prepared from Ti6Al4V-50%TiB2 mixture), the significant improvement in wear resistance of the composites are attributed to the reduced amount of plastic deformation resulting from improved bulk hardness of composites upon TiB2 addition.

The different performance of hardness and tribological property from opposite side makes the produced FGM good candidates in many favoured regions. For example, in the machine where good tribological property is needed, the composite side can be the working face, while the metal side can be better connected (such as by welding) with the moving part of the machine.

4. Conclusions
Functionally gradient Ti6Al4V-TiB composite with smooth layer transition was produced from powder mixtures with different ratio of Ti6Al4V and TiB2 by spark plasma sintering. SEM and XRD analyses showed the in-situ TiB formation, which plays a key role on microstructure, hardness and tribological behavior of the composite.

A significant reduction in wear and CoF values was noted due to an increase in TiB phase in the sintered samples (as a result of increase in TiB2 content in powder mixtures). The increase of hardness of the composites upon TiB inclusion is held responsible for it.

Acknowledgements
This work was supported by the Estonian Research Council grants PRG643 (I. Hussainova), M-ERA.Net project “HOTselflub” MOBERA18 N.20097582-CA and “DuraCer” MOBERA9 ETAG18012.

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