Hot isostatic pressing of in-situ TiB/Ti-6Al-4V composites with novel reinforcement architecture, enhanced hardness and elevated tribological properties

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Abstract

In this study, titanium borides reinforced Ti-6Al-4V composites have been successfully prepared by hot isostatic pressing (HIPing). The microstructure of the as-fabricated samples was investigated using X-ray diffraction (XRD) technique, secondary electron microscopy (SEM) and electron backscatter diffraction (EBSD) and the mechanical properties evaluated through microhardness and wear resistance measurements together with nano-indentation. It was found that during HIPing the additive particles TiB_2 have transformed into TiB needles which tend to decorate at prior particle boundaries of the consolidated powder particles to form a network structure. Under the same HIPing condition, the needles became increasingly coarser and agglomerated with increased addition of TiB_2. Meanwhile, a large population of TiB needles have grown into the prior particle matrix, which is believed to be beneficial to the bonding between particles. The micro-hardness of the synthesised materials increased with increased volume fraction of TiB. Nano-indentation measurement demonstrates that the TiB network structure shows much higher nanohardness than the surrounding matrix regions. The friction coefficient of the synthesised composites decreased continuously with increased volume fraction of TiB, indicating improved wear resistance. High resolution transmission electron

microscopy (HRTEM) analysis on wear debris revealed the formation of a series of oxides suggesting that chemical reaction between alloy elements and oxygen in air may have happened. It is thus concluded that the wearing of the current samples is a result of both friction and chemical reaction.

Key words: Hot isostatic pressing; titanium matrix composites; microstructure; microhardness; wear properties

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1. Introduction

Titanium alloys are well known for their high specific strengths (high strength-to-weight ratio) and excellent corrosion properties. A number of efforts have been made to further improve various properties (such as strengths, wear resistance and high temperature properties) of these materials by introducing reinforcement particles into them. The common reinforcement materials include B_4C, SiC, TiC, Ti_5Si_3, CrB and TiB_2. Compared with many other reinforcement materials, TiB_2 shows similar density and good thermal compatibility with titanium (similar thermal expansion coefficients) and has been proven to be effective in strengthening titanium alloys. It has thus been widely used as reinforcement particles for titanium alloy based composites produced by different techniques. Gorsse et al [1] developed Ti-6Al-4V composites reinforced with large volume fractions of TiB (20-40%) by hot isostatic pressing (HIPing) of ball milled Ti-6Al-4V and TiB_2 powder particles. The as-HIPed microstructure was characterized by randomly aligned TiB needles/whiskers in the matrix but did not result in obvious improvement in tensile properties. Attar et al [2] synthesised in-situ titanium-titanium boride composites by selective laser melting (SLM) of ball milled Ti-TiB_2 powder particles. During solidification and cooling after SLM, very fine needle-like TiB particles were formed and homogenously distributed among the alloy matrix, which led to significant improvement in compressive strengths. Huang et al [3-9] developed a series of titanium borides reinforced titanium alloy composites by hot pressing or sintering of milled mixture of titanium alloy powder and TiB_2. They have demonstrated the in-situ formation of TiB network structure along prior particle boundaries (PPBs) in the synthesised titanium alloy composites and the significant improvement in room temperature strengths due to the presence of the network structure. Particularly, they even found that the presence of TiB network structure is beneficial for high temperature strengths [10]. This is contradictory with conventional belief that PPBs decorated by precipitates are harmful for mechanical properties of materials synthesised by powder metallurgy, especially high temperature mechanical properties such as strengths, ductility, creep rupture and

fatigue [11-22]. It is obvious that for applications, more studies are required to comprehensively investigate the mechanical properties of titanium alloy composites with this kind of network structure.

In this study, given that titanium alloys usually show relatively poor tribological properties such as high and unstable coefficients of friction, low abrasive and adhesive wear resistance, we will focus on the investigation on the surface properties of titanium borides reinforced composites such as microhardness, friction and wear properties. To the best knowledge of the authors, the work on surface properties of titanium alloy composites with titanium boride network structure is lacking. More work is also under way to comprehensively evaluate the high temperature mechanical properties of this type of materials. HIPing has been employed to synthesise titanium borides reinforced composites in the present study as HIPing can give 100% density eliminating any negative effects caused by porosity that are usually present in sintered or hot pressed materials [4-5]. Advanced materials characterization techniques such as SEM together with EDX, transmission electron microscope (TEM) and high resolution transmission electron microscope (HRTEM) have also been used to characterize the synthesised materials before and after wear testing to understand the wear mechanism of these materials.

2. Experimental

2.1 Materials and powder mixing

Plasma atomized Ti-6Al-4V powder produced by BaoJi Haibao Special Metal Materials Company, China and TiB_2 powder produced by Aladdin Industrial Corporation, China, have been used in the current study. The as-received Ti-6Al-4V and TiB_2 powder show a particle size range of 70-150μm and 3-5μm, respectively. The Ti-6Al-4V and TiB_2 powder particles with different weight percentages (0%, 3 wt.%, 5 wt.%, and 8 wt.% TiB_2) were then mixed by ball milling. Steel balls with a ball-to-powder weight ratio of 4:1 have been used for the powder mixing. The milling

process was conducted at a rotation speed of 200 rpm and the milling duration was set up to 4 hours for each mix.

2.2 Powder HIPing

The mixed powder particles were then consolidated by HIPing. SAE 1045 steel capsules with an internal diameter of 60 mm, a length of 150 mm and a wall thickness of 2 mm were made and used to contain the mixed powder particles before being outgassed and sealed. Outgassing was conducted overnight with preheat treatment of the capsules at 600°C, leading to acquisition of a vacuum above 1×10^{-3} Pa. The samples were then HIPed at 1200 °C and 120 MPa for 3 h prior to furnace cooling using a QIH-15 HIP machine made by ABB Company, USA.

2.3 Microstructural characterisation

The as-HIPed samples were then sectioned, ground and polished for X-ray diffraction (XRD) using a XRD-7000S diffractometer for phase identification. The XRD machine operated with a Cu anticathode (λ=1.5406 Å) at 35 kV and 40 mA using a continuous scan mode. A quick scan was first conducted at 5 º/min over a wide range of 2θ (20-80º) to give a general overview of the diffraction peaks. Then, a slower scan at 0.5 º/min was performed between 41.0-42.5º for 2θ to obtain a more accurate identification of diffraction peaks corresponding to TiB. The as-polished samples were then etched in Kroll reagent (2% HF, 6% HNO_3 and 92% H_2O) for 20s prior to microstructural characterization using a scanning electron microscope (SEM, JSM-7600F, Japan) fitted with an energy dispersive spectroscopy detector (EDX). Electron backscatter diffraction (EBSD) technique was also used to characterize the microstructure of samples fabricated.

2.4 Mechanical testing

To understand the surface properties of the as-fabricated materials, a wide range of surface property measurement techniques have been used. Microhardness measurement was performed on the as-HIPed samples using a Vickers tester (430SVD,

Wilson Hardness, USA). A load of 3 Kg and a dwell duration of 15 s have been used for each measurement. Nano-indentation tests were also conducted using a high-precision nano-hardness scratch tester (TI750, Hysitron, USA) and a load of 8000 mN and a dwell duration of 2 s were used for each test. Wear tests were carried out in air and at room temperature using a ball-on-plate tribometer (CETR-UMT-2, USA). The tests involved the use of a ball made from Si_3N_4 with a diameter of 6.35 mm to slide against as-polished flat specimen surfaces following a linear back and forth motion under a non-lubricated condition. A sliding distance of 15 mm, a sliding speed of 10 mm/s, a load of 60 N and a total back-and-forth sliding duration of 60 min have been used for each test. The coefficient of friction (COF) was dynamically recorded at an acquisition rate of 12 points/min using a computer. The profiles of the worn tracks were measured using a confocal scanning optical microscope (Micromeasure2, France) and the surface structure of each sample and the wear debris after wearing testing were examined using SEM together with EDX (Sirion 200, Holland). Transmission electron microscopy (TEM) and high resolution TEM using a FEI Tecnai G2 F30 TEM microscope were also applied to characterize the wear debris. The HRTEM micrographs were analysed using DigitalMicrograph software and the ananlysis results such as spacing between atomic planes were compared with XRD database to identify phases present in the as-fabricated samples.

3. Results

3.1 Powder characterisation

Fig. 1 shows the particle distribution and morphology of as-received plasma atomized Ti-6Al-4V powder. It is obvious that the powder particles are characterised by a very much single particle size mode with a typical particle diameter range of 100-130μm. These particles show a highly spherical morphology without many satellite particles attached to them. After being mixed with TiB_2 particles, the Ti-6Al-4V powder particles still remain spherical probably due to relatively short mixing duration (4h) used in the current study but seem to show a rougher surface than the as-received

counterpart due to the decoration of TiB_2 particles; see Fig.2. Moreover, it is obvious that the additive TiB_2 particles have been homogeneously distributed on the Ti-6Al-4V powder particle surfaces. With increased addition of TiB_2, more TiB_2 particles decorating on the Ti-6Al-4V powder particle surfaces could be observed.

3.2 Microstructure of as-HIPed samples

Fig. 3 shows the XRD analysis results for the as-HIPed Ti-6Al-4V+TiB_2 samples. Apart from the presence of α-Ti, some peaks corresponding to TiB can be observed. The presence of TiB instead of TiB_2 suggests that the added TiB_2 may have reacted with Ti matrix during the high temperature HIPing to form TiB. SEM imaging was also employed to study the microstructure of the as-HIPed samples in detail and the results are shown in Fig. 4. It is clear that the microstructure of the synthesised composites has been dominated by TiB needles decorating along PPBs, leading to the formation of a TiB network structure throughout the samples. This is in contrast to the as-HIPed Ti-6Al-4V sample where no obvious PPB can be seen. Moreover, the (α+β) lamellar structure is much more developed in the TiB-free sample than in the TiB-containing samples, with many of the α and β laths extending longer than 150 μm in the former, suggesting that obvious grain growth may have happened in the TiB-free sample during HIPing. The α and β laths in the TiB-containing samples are much shorter (<50 μm) with α laths being much wider and have obviously been confined by the TiB network developed. As a result, the aspect ratio of α laths in the TiB-containing samples is smaller than those in the TiB-free sample. This observation is consistent with EBSD analysis where a number of short and wide α laths can be observed and these laths tend to show random orientations; see Fig. 5. Moreover, a number of equiaxed α laths can be observed. In addition, it is noted that with increased volume fraction of TiB_2, the TiB network becomes increasingly larger and integrated; see Fig. 6. This is suspected to be due to that with more and denser TiB along the PPBs, the coalescing between TiB particles may have been strengthened. While a large population of TiB needles line up along PPBs, there are also a large number of TiB needles growing into the prior powder particles, i.e., growing across

PPBs to act like bridges between two neighboring particles; see Fig. 6 (d) and (f). This kind of alignment of TiB needles is believed to be beneficial for the inter-particle bonding.

3.3 Mechanical properties

Fig. 7 shows the variation of micro-hardness of the as-HIPed samples with the varied addition of TiB_2. It is clear that the micro-hardness of the HIPed samples increases continuously with increased volume fraction of TiB_2. Nano-indentation test has also been performed across a TiB network region between two neighboring prior particles and the results are shown in Fig. 8. It can be seen that the TiB network structure shows much higher nano-hardness than the surrounding matrix regions, suggesting that the PPBs could be hardened/strengthened by the presence of this kind of network structure. Fig. 9 shows the friction testing results of the samples fabricated. The coefficient of friction was found to decrease steadily with increased TiB_2, indicating improved wear resistance with increased addition of TiB_2.

The sample surfaces after friction testing were further investigated using SEM and EDX and the results are shown in Fig. 10 and Fig. 11. It can be seen that the as-HIPed Ti-6Al-4V sample shows a predominant worn and damaged surface whereas samples containing TiB network structure demonstrate a number of smooth regions/islands throughout their sample surfaces where the materials still remain relatively compact and intact. These smooth regions are in shark contrast with their neighboring regions where a lot of debris were observed indicative of serious wearing; see Fig. 10. Moreover, it is noted that with increased addition of TiB_2, both the number and area fraction of this kind of smooth regions increase correspondingly indicating improved wear resistance, which is consistent with above wear testing results. EDX analysis on some smooth regions and worn regions on the surfaces of TiB-containing samples reveals the presence of boron (aslo see Table 1), suggesting that both the matrix region and the TiB network have experienced wearing damage during the friction testing. Si was also detected on the TiB-bearing sample surfaces after the friction test

which is obviously from the tooling material (Si_3N_4). However, no Si was detected on the surface of TiB-free sample, further suggesting that the TiB-containing samples show better wear resistance. Pronounced peaks corresponding to oxygen were also observed implying that there may be some oxides present.

Wear debris from different samples was further analyzed using SEM+EDX, TEM and HRTEM. The results are shown in Fig. 12 and Fig. 13. Again, Si was detected in the wear debris from the TiB-containing samples but is absent in the debris from TiB-free sample (Fig. 12). This further confirms that the presence of TiB network structure has indeed improved the wear resistance of the titanium alloy. HRTEM analysis on the wear debris reveals more products present. A number of oxides such as $Ti(BO_3)$, TiO_2, TiO, V_2O_5, Al_2O_3, SiO_2 and B_2O_3 were identified to be present. It is obvious that these products are the result of reaction between elements in these samples and the oxygen in air. The reaction may have been triggered and promoted by the heat buildup due to dry friction between samples and tooling. The presence of Si (due to wear of tooling) in the form of SiO_2 confirmed by the HRTEM analysis further indicates the superior wear resistance of TiB-containing composites as compared with the TiB-free sample.

4. Discussion

The current experimental results have clearly demonstrated that the added TiB_2 particles have transformed into TiB needle structure after high temperature HIPing. This is believed to be due to the reaction between TiB_2 and Ti-6Al-4V alloy matrix ($TiB_2 + Ti \rightarrow 2TiB$). Most of the TiB needles have contributed to the formation of a network structure along PPBs which has been found to harden/strengthen PPBs (Fig. 8(b)) while a large population of TiB needles were found to grow into the prior particle matrix acting as bridges between neighboring particles, which will be undoubtedly benign for the inter-particle bonding. Moreover, the network structure was shown to have confined the growth of ($\alpha+\beta$) lamellar structure and the grains within each prior particle as evidenced by Fig. 4. All of these factors may have

contributed to the overall improvement of strengths of this type of metallic composites at both room temperature and high temperatures [3-10]. With the use of HIP in the current study, no porosity like those present in sintered or hot pressed samples [4-5] was observed and thus it is believed that related mechanical properties can be further improved.

Indeed, the unique microstructure developed in the current study has been demonstrated to exhibit superior surface properties such as microhardness and wear resistance in comparison with the Ti-6Al-4V sample. With increased addition of titanium borides, both microhardness and wear resistance increased continuously (Fig. 7 and Fig. 9). The friction mechanism seems to be highly complicated as it involves a lot of chemical reaction between the elements within the specimens and the oxygen in air, evidenced by the formation of a number of types of oxides (Fig. 13). This kind of chemical reaction was obviously initiated and promoted by the heat generated due to friction. In turn, the chemical reaction may have promoted wearing of these samples as a lot of the debris turns out to be the product of this kind of chemical reaction. It is thus reasonable to believe that the wearing of the current samples is a result of combined effects from both mechanical friction and chemical reaction. Moreover, it is noted that Si from the tooling material is present in the surface and debris of TiB-containing composites but absent in those of TiB-free sample, further suggesting that the TiB-containing composites show better wear resistance than the titanium alloy itself.

5. Conclusions

- High temperature HIPing led to transformation of the fine additive TiB_2 particles into TiB needles at prior particle boundaries to form a network structure.
- A large population of TiB needles have grown into prior particle matrix acting as bridges between neighboring powder particles after HIPing.

- The TiB network structure shows much higher nanohardness than the surrounding matrix regions.
- Both micro-hardness and wear resistance of the synthesised composites increased with increased volume fraction of TiB.
- The wearing of the current samples is a result of both mechanical friction and chemical reaction.

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