Investigation on Microstructure and Hardness of In-situ (TiB+TiC)/Ti Composite Prepared by Selective Laser Melting

Dong Zhu¹, Liang Zhang²,²*, Wenheng Wu²,², Lin Lu²,², Jia Song²,², Xiaoping Ni²,², Wenhua Zhu¹, Jinneng Zhao¹,², Sunwang Gu¹ and Xiaolong Shan⁵

¹Faculty of Engineering, Shanghai Polytechnic University; Shanghai 201209, China; ²Shanghai Research Institute of Materials, Shanghai 200437, China; ³Shanghai Engineering Research Center of 3D Printing Materials, Shanghai 200437, China; ⁴ZTT SRIM Additive Manufacturing Co., Ltd, Nantong 226000, China; ⁵Shanghai Zhongtian Aluminum Wire Co., Ltd, Shanghai 201100, China; *E-mail: liangustb@126.com

Abstract. This paper aims to research the influence of the addition of boron carbide ceramic particle enhancer on the grain shape and microstructure of commercially pure titanium (CP-Ti) during laser additive manufacturing process. It is found that during SLM process of B₄C/CP-Ti, the reinforced particles B₄C react with CP-Ti to produce prismatic TiB and whisker-like TiB and granular TiC. The in-situ synthesized TiC and TiB extremely improve the microhardness of the SLM-processed Ti composite from 213.9 to 513 HV₀.₅, but drastically reduced its plasticity in comparison to CP-Ti, which is of great significance for further popularization of titanium matrix composites.

1. Introduction
Titanium and titanium alloys have outstanding advantages such as low density, high strength, corrosion resistance and oxidation resistance[1-2]. They are extensively used in modern industries such as aerospace, chemical engineering, marine engineering and major national defense equipment. In particular, commercially pure titanium (CP-Ti) is the most widely used titanium-based material in the biomedical field[3-4]. Compared with Ti-6Al-4V, it does not contain harmful elements such as Al and V[5-6], and has better biocompatibility. But the application and further development of CP-Ti are limited by its relatively low the wear resistance and hardness[7-9].

In order to overcome the drawbacks of CP-Ti, reinforcing particles are usually added to titanium matrix for preparing titanium-based composite material, which is expected to improve the hardness and wear resistance of titanium alloys. However, due to the high price of SiC fiber and B fiber, and the difference in thermal expansion coefficient with the titanium matrix, the application of continuously reinforced titanium matrix composite materials are limited, on the other hand, the traditional ingot metallurgy and powder metallurgy methods for preparing titanium-based composite materials have numerous disadvantages, such as complicated processing technology, low production efficiency, high energy consumption, and uncontrollable enhanced phase distribution.

In recent years, selective laser melting (SLM) emerges as one of the most promising metal additive manufacturing (AM) technologies. Compared with traditional manufacturing process, it has extraordinary capability of fabricating complex-shaped parts, design flexibility, high customization, and no need of assembly or molds. The advantages of AM have been widely used in aerospace, automobile manufacturing, medical and other fields[10].

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd
Several researchers manufactured titanium-based composite materials by SLM technology, and achieved good reinforcement effects. Li et al.[11] SLMed B4C/TC4 titanium composite material, whose surface density reached 99%, and compared with the TC4 molded parts, the Vickers hardness and tensile strength increased about 45% and 26%, respectively. Gu et al.[12] found that the hardness and elastic modulus of TiC-reinforced titanium-based materials were 22.7 and 2.4 times that of titanium alloy, and the wear resistance was greatly improved as well. He et al.[13] investigated the influence of TiC on the microstructure and properties of CP-Ti and found that evenly distributed TiC, as nucleation points, promoted the nucleation and growth of α-Ti grains, which significantly improved the tensile strength of titanium alloy. Zhou et al.[14] studied the corrosion resistance of SLMed TiN/CP-Ti and discovered that the TiN reinforced particles restricted the growth of α-Ti grains, making the grains more refined and generated a TiO2 passivation film on the surface, improving the corrosion resistance of CP-Ti.

Boron carbide (B4C) is one of most commonly used reinforcing particles to improve strength, hardness and wear resistance of titanium alloys[15]. Lu et al.[16-17] prepared Ti-TiB-TiC in-situ autogenous titanium matrix composites by self-propagating high-temperature synthesis reaction between titanium and boron carbide. The whisker-like TiB and the equiaxed TiC were obtained, which enhanced creep resistance. Attar et al.[18] prepared CP-Ti samples reinforced by TiB2 ceramic particles under SLM molding process. The results showed that in-situ TiB crystals were generated in-situ in α-Ti matrix, and the strength and elastic modulus of CP-Ti increased 2-3 times. In-situ autogenous particle reinforced composites have outstanding advantages compared with externally added particle reinforced composites: (1) heat treatment will not produce other precipitates because of good thermodynamic stability; (2) stable interface, no reactants existence; (3) The reinforcement is finer in size, more uniform in the matrix, and it has excellent mechanical properties.

In this study, the bulk-form B4C/Ti composite with novel microstructure under various processing conditions are successfully manufactured by SLM. Considering influence of energy penetration of powder-bed on microstructure of SLM-processed B4C/Ti composite, the densification response, elements distribution state surrounding B4C reinforcements and microstructure characters of the composite with various laser powers are then analyzed in detail. Finally, the evolution mechanism of microstructure under variable laser power is experimentally concluded.

2. Experimental Procedures

2.1. Powder Preparation
In this experiment, the spherical pure titanium powder with a particle size of 15~53 μm and the B4C ceramic particles with a particle size of 5 μm are mixed by ball milling to obtain a uniform distribution of the titanium based composite powder. The comparison of powder morphology before and after ball milling is shown in Fig.1.
2.2. Experimental Equipment and Measurements Procedures
SLMed samples are performed on a level Ti substrate plate using EOS M290 device. The device has a Yb-fibre fiber laser with a maximum power of 400 W and a spot diameter of 50-150 μm. The powder layer thickness is set to 0.02 mm and the other processing parameters are shown in Table 1 during SLM titanium base composite powder. The substrate temperature is initially heated to 150 °C. The bulk-form composite samples with a three dimension of 15 mm*15 mm*15 mm are then fabricated in a layer-by-layer manner. Throughout the SLM process, high-purity Ar is used as a shielding gas to keep the concentration of O2 below 0.8%.

| Laser power (W) | Hatch spacing (mm) | Scanning speed (mm/s) |
|----------------|--------------------|-----------------------|
| 280            | 0.05               | 1000                  |
| 280            | 0.05               | 1200                  |
| 280            | 0.05               | 1600                  |
| 280            | 0.1                | 800                   |
| 280            | 0.1                | 1000                  |
| 320            | 0.05               | 1000                  |
| 320            | 0.05               | 1200                  |
| 320            | 0.1                | 1000                  |
| 320            | 0.1                | 1200                  |
| 350            | 0.05               | 1200                  |

The samples for metallographic characterization test is carried out by a conventional method. Firstly, side surface (Y-Z plane) of the sample is subjected to conventional grinding, polishing and etching treatment. Secondly, the treated surface is corroded for 10 s by the corrosive reagent, a mixed acid solution of hydrofluoric acid and nitric acid (10 ml HNO₃, 5 ml HF and 85 ml H₂O). At last, the cross-sectional microstructure of samples is examined by an optical microscope. In addition, we also observe microstructure by a scanning electron microscope and test Microhardness by a vickers hardness tester with 4.9 N load and 10 s dwelling time.

3. Experimental Results and Analysis
As shown in Fig. 2, there is little change in the particle size distribution before and after the ball milling and mixing of the powder. Combinated with the micro morphology (Fig. 1), it can be inferred that the B₄C particles are attached to the surface of the spherical titanium particles.

![Figure 2. The particle size distribution of TA2 and TA2+B₄C](image-url)

Table 1. SLM process parameters used in the experiment
3.1. Effect of Component Addition on the Hardness of the Sample

According to our SLM experiments, we find that under small volume energy density, the titanium base composite powder cannot be formed. This can attribute to the melting point of B₄C is higher than that of CP-Ti. Thus, we select these samples with relatively better forming quality and the results are shown in the Fig. 3. It can be seen that after the addition of boron carbide particles, the microhardness of B₄C/CP-Ti increases from approximately 213.9 HV₀.₅ to 513 HV₀.₅ (Fig. 2). In addition, we also find that the volume energy density take little effect on the microhardness of CP-Ti and B₄C/CP-Ti. This is because that according to the reaction equation B₄C+Ti→TiC+TiB, TiC and TiB reinforcing phases can be formed by the in-situ reaction between boron carbide and CP-Ti. The dispersed distribution of TiC and TiB can refine grains and improve microhardness.

![Figure 3. The effect of component addition and energy density on the hardness of the samples](image)

3.2. Influence of Component Addition on the Microstructure of the Sample

In order to further explore the reasons of the increase in hardness, the microstructure of the sample is investigated by means of a scanning electron microscope. The microstructures after corrosion are shown in the Fig. 4.
Compared microstructure of CP-Ti before and after adding reinforced boron carbide particles, it can be clearly seen that the addition of boron carbide increases fineness of CP-Ti, and precipitates prismatic TiB and whisker-like TiB and granular TiC. The partial enlargement of the diagram (b) is shown in the Fig. 4c, there are prismatic shape phases and needle-like precipitate phases. Combining with the results of SEM and EDS analysis, it can be confirmed that the precipitated phase of TiB is surrounded by the granular precipitate phase of TiC (showed in Fig. 4c). Fig. 5 describe the B_{4}C in-situ autogenous reaction process. When the high-energy laser acts on the surface of the powder, because the melting point of TA2 is lower than that of B_{4}C, B_{4}C is wrapped by the liquid phase TA2, as shown in Fig. 5a. With the mutual diffusion of B, C and Ti, equilibrium conditions are established at the interface, and whisker TiB and granular TiC are precipitated on the surface. Owing to the rapid solidification of the molten, if larger B_{4}C particles marked red fail to react completely, otherwise the reaction can proceed completely without B_{4}C particles remaining. Similar B_{4}C residual phenomenons are also mentioned in the researchs of Xia and Fereiduni [19-20].
Figure 5. The schematic interaction between B$_4$C particles and liquid TA2 (a) liquid TA2 and solid B$_4$C, (b) interdiffusion between the B$_4$C and liquid TA2, (c) formation of solid and liquid layers with equilibrium C$_S$ and C$_L$ concentrations, respectively at the solid/liquid interface, (d) precipitating whisker-like TiB and granular TiC on the surface of B$_4$C.

4. Conclusions
In this study, the in-situ synthesized (TiC+TiB)/CP-Ti composite is directly fabricated using SLM from the mixed B$_4$C/CP-Ti powder system. The important results are summarized as follows:

1. After the ball milling, the B$_4$C particles are attached to the surface of the spherical CP-Ti particles, and the particle size distribution of B$_4$C/CP-Ti is almost same as that of CP-Ti.

2. During SLM process, the reinforced particles B$_4$C react with CP-Ti to produce prismatic TiB and whisker-like TiB and granular TiC. The in-situ synthesized TiC and TiB significantly improve the microhardness of the SLM-processed Ti composite up to 513 HV$_{0.5}$, but drastically reduced its plasticity in comparison to CP-Ti.

5. Acknowledgments
This work is supported by the project to Shanghai Rising-star program (Project Number 18QB1400600), Shanghai Polytechnic University Graduate Project Fund (Project Number EGD19YJ0086), and Cooperative Development Project (Project Number 18ZTSC-01).

6. References
[1] Zhu Y, Liu D and Tian X: Mater. Des Vol. 56 (2014), p. 445-453
[2] Carroll B E, Palmer T A and Beese A M: Acta Mater Vol. 87 (2015), p. 309-320
[3] Alves V A, Reis R Q and Santos I C B: Corros Sci Vol. 51 (2009), p. 2473-2482
[4] J.E.G González and Mirza-Rosca J C: J. Electroanal. Chem Vol. 471 (1999), p. 109-115
[5] Brailovski V, Prokoshkin S and Gauthier M: Mater. Sci. Eng. C Vol. 31 (2011), p. 643-657
[6] Fukuda A, Takemoto M and Saito T: Acta Biomater Vol. 7 (2011), p. 1379-1386
[7] Banerjee D and Williams J: Acta Mater Vol. 61 (2013), p. 844-879
[8] Attar H, Calin M and Zhang L C: Mater. Sci. Eng. A Vol. 593 (2014), p. 170-177
[9] Attar H, Prashanth K G and Chaubey A K: Mater. Lett Vol. 142 (2015), p. 38-41
[10] Saeid Ghesmati Tabrizi, Seyed Abdolkarim Sajjadi, Abolfazl Babakhani and Weijie Lu: Mater. Sci. Eng. A Vol. 624 (2015), p. 271-278
[11] Hailiang Li, Zhihua Yang, Delong Cai and Dechang Jia: Mater. Des Vol. 185 (2020)
[12] Dongdong Gu, Yves-Christian Hagedorn, Wilhelm Meiners, Konrad Wissenbach and Reinhart Poprawe: Compos Sci Technol Vol. 71 (2011), p. 1612-1620
[13] Beibei He, Kun Chang, Wenheng Wu and Cailin Zhang: Vacuum Vol. 143 (2017), p. 23-27

6
[14] Shengfeng Zhou, Yu Zhao, Xiaojian Wang, Wei Li, Dongchu Chen and T.B. Sercombe: J. Alloys Compd. Vol. 820 (2020)
[15] Sun Youhong, Zhang Chi, He Linkai, Meng Qingnan and Liu Bao-Chang: Sci. Rep. Vol. 8 (2018), p. 11104
[16] Lu W J, Wu R J and Zhang D: Compos Interfaces Vol. 9 (2002), p. 41-50
[17] Lu W J, Zhang D and Zhang X: Scr. Mater. Vol. 44 (2001), p. 2449-2455
[18] Attar H, LöBer L and Funk A: Mater. Sci. Eng. A Vol. 625 (2015), p. 350-356
[19] Mujian Xia, Aihui Liu, Zhiwei Hou, Nianlian Li, Zhong Chen and Hongyan Ding: J. Alloys Compd. Vol. 728 (2017), p. 436-444
[20] Eskandar Fereiduni, Ali Ghasemi and Mohamed Elbestawi: Mater. Des Vol. 184 (2019)