**Rare Metal Materials and Engineering**
Volume 47, Issue 3, March 2018
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com

ScienceDirect

**Cite this article as:** Rare Metal Materials and Engineering, 2018, 47(3): 0788-0793.

ARTICLE

# Effects of Ti Sheet Insert on Microstructure and Properties of Graded Composites of $TiB_2$-based Ceramic and Ti-6Al-4V Alloy

**Chen Shuo, Zhao Zhongmin, Zhang Long, Cheng Zhaogang, Yu Guibo**

*Special Ceramics Laboratory, Army Engineering University, Shijiazhuang 050003, China*

**Abstract:** By inserting Ti sheet between ceramic powder and Ti alloy steel, ($TiC-TiB_2$)/Ti-6Al-4V graded composites were rapidly prepared by SHS centrifugal-casting process with different Ti sheet thickness from 0.5 to 1.5 mm. XRD, FESEM and EDS results show that there is no significant change in phase composition of the ceramic matrix after inserting Ti sheet, but the inserting promotes the microstructure refinement of the reaction products with the thickness increasing. Meanwhile, the introduction of Ti sheet not only enhances the thickness of the gradient interface, but also decreases the thermal infected zone of interface. Moreover, fusion bonding and atomic interdiffusion between liquid $TiC-TiB_2$ and excessive Ti liquid in thermal vacuum circumstances are considered to initiate peritectic reaction of $TiB_2(s) + Ti(l) \rightarrow 2TiB(s)$, direct growth of TiB solids from liquid Ti and eutectic reaction of TiB solids and liquid Ti at the final stage of joint solidification, so that consumption of $TiB_2$ solids and increase of TiB crystal relieve the interface residual stress, and the joint of the ceramic to Ti alloy is achieved in multilevel and multi-scale microstructure. The joint represents a transitional change in Vickers hardness and gets a high shear strength of ($316\pm25$) MPa between the ceramic and Ti alloy.

**Key words:** graded composite; self-propagating synthesis; interfacial microstructure; atomic interdiffusion; thermal match

$TiC-TiB_2$ composite ceramics have attracted significant attention due to their promising potential in engineering applications under extreme conditions for their excellent combination of mechanical and electrical properties as well as their good corrosion and oxidation resistance at high temperature[1]. But traditional ceramics have low toughness and are hard to manufacture complex parts. Therefore, it is necessary to manufacture these complex parts by joining ceramics and metals to meet the special requirements[2]. Hence, various ceramic-metal joining techniques have been developed and improved over the past 50 years, such as mechanical joining, adhesive joining, microwave joining, ultrasonic welding, explosive welding, combustion reaction joining, field-assisted bonding, diffusion bonding, transient liquid phase bonding and partial transient liquid phase bonding[3]. Among them, diffusion bonding and reactive metal brazing have been explored most extensively, whereas the partial transient liquid phase bonding with the advantages of brazing and diffusion bonding is a promising technique[3,4].

However, it is generally known that a key problem in joining ceramic and metal is the thermal expansion mismatch between them, which brings about high residual stress at the interface of the ceramic and the metal, thereby resulting in either cracking of the ceramic or poor strength of the joints. As a result, functionally graded joints between ceramics and metals offered a solution to the thermal stress problem and have brought a wide interest[5,6]. Recently, a rapid and economical processing named self-propagating synthesis centrifugal-casting process has been applied to prepare bulk solidified $TiC-TiB_2$ ceramics and laminated composite materials of $TiC-TiB_2$ ceramics and Ti alloy successfully[6-8]. However, there are some visible $Al_2O_3$ inclusions in the ceramics when ($CrO_3$+2Al) subsystem is added as the

Received date: March 15, 2017
Foundation item: National Natural Science Foundation of China (51072229, 51502338)
Corresponding author: Zhao Zhongmin, Ph. D., Associate Professor, Special Ceramics Laboratory, Army Engineering University, Shijiazhuang 050003, P. R. China, Tel: 0086-311-87994683, E-mail: zhaozm2007@aliyun.com

activator, which will seriously deteriorate the flexural strength of the materials. Meanwhile, uncontrollable heat concentration is easy to melt-through the Ti alloy substrate.

In this paper, a preheating process was suggested to avoid the $Al_2O_3$ inclusions instead of the ($CrO_3$+2Al) subsystem. Meanwhile, Ti sheet was introduced between ceramic powder and Ti alloy steel. On the one hand, the melting heat consumption of the Ti sheet would control heat accumulation against the melt-through of the substrate. On the other hand, the molten Ti sheet would increase the concentration of the Ti liquid between the ceramic and Ti alloy, which initiated peritectic reaction and eutectic reaction to produce more TiB solids. Therefore, novel graded (TiC-$TiB_2$)/Ti-6Al-4V composites were achieved by inserting different thickness Ti sheet, and microstructure as well as mechanical properties of the materials was discussed. Meanwhile, effects of Ti sheet for modifying the joint and improving the properties of the composite were investigated.

## 1 Experiment

Raw materials were prepared from high purity (>97%) $B_4C$ powder with particle size less than 3 μm and high purity (>99%) Ti powders with particle size less than 34 μm. The molar ratio (Ti to $B_4C$) of 3:1 was chosen as the starting composition based on Eq.(1), so the composition of the solidified TiC-$TiB_2$ composite was determined as TiC-66.7 mol% $TiB_2$. In order to improve the adiabatic combustion temperature, preheating process of 200 °C was introduced for increasing adiabatic combustion temperature.

$$3Ti+B_4C \rightarrow TiC+2TiB_2 \qquad (1)$$

The above powder blends were mechanically homogenized by ball milling for 2 h. The Ti-6Al-4V plate with the thickness of 10 mm was placed at the bottom of the cylindrical graphite crucible as a substrate, and its chemical composition is Ti-6.03Al-4.24V-0.096Fe-0.15O-0.01N-0.0006H (wt%). Then the crucible was filled with the mechanically-activated raw blends (2.0 kg) at constant pressure and Ti sheet with 75 mm in diameter under different thickness from 0.5 to 1.5 mm was inserted between the powder mixture and Ti alloy substrate. After that, the prepared graphite crucibles were fixed on the centrifugal machine. The combustion reaction was triggered with the electrical heat W wire (diameter of 0.5 mm) while the centrifugal machine provided a high-gravity acceleration of 2000*g* ($g$=9.8 m/$s^2$, where $g$ means the gravitational constant). When the combustion reaction was over, the centrifugal machine continued to run for 30 s. As the combustion chambers were cooled to ambient temperature, the graphite crucibles were taken out of the combustion chambers. Finally, graded composites of (TiC-$TiB_2$)/Ti-6Al-4V with 90 mm in diagonal were obtained after grinding, as shown in Fig.1.

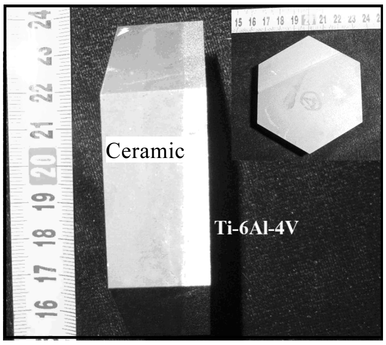


Fig.1 Macrography of TiC-$TiB_2$/Ti-6Al-4V graded composites

The phase composition was identified by X-ray diffraction (XRD) with a step of 0.02° and a scanning rate of 2 °/min. The microstructure of the composite and fracture morphology were examined by field emission scanning electron microscopy (FESEM). Electron probe microanalysis (EPMA) was conducted by energy dispersive spectrometry (EDS).

The hardness of the composite was measured using Vickers hardness tester (HV5) under 196 N load. Meanwhile, the composites of TiC-$TiB_2$ ceramic and Ti alloy steel were cut and ground into six rectangular bars measuring 8 mm (width) × 5 mm (height) × 20 mm (length) for determining the interlaminar shear strength, and the interlaminar shear strength was evaluated by the equation $\tau=P/A$, where $\tau$ is the interlaminar shear strength of the joint, $P$ is the actual breaking load and $A$ is the initial area of samples.

## 2 Results and Discussion

### 2.1 Effects of Ti sheet insert on the ceramic matrix

Fig.2 shows the X-ray diffraction patterns of the ceramic matrix of (TiC-$TiB_2$)/Ti-6Al-4V graded composites prepared by appending Ti sheet with different thickness. It is obvious that the phases in the products are $TiB_2$ and TiC. Comparing the X-ray diffraction patterns of $TiB_2$ and TiC in Fig.2a~2d, no remarkable difference in phase composition of the ceramic matrix under different thickness of Ti sheet was spotted.

FESEM micrographs of the ceramic matrix show that a large number of randomly orientated, fine $TiB_2$ platelets (presented by the dark areas in Fig.3) are uniformly embedded in the irregular TiC grains (presented by the grey areas in Fig.3). Apparently, the volume fraction of irregular TiC grains increase as the thickness of Ti sheet increases in Fig.3a~3d. In addition, with the increase of the thickness of Ti sheet, the grain size of $TiB_2$ platelets becomes more homogeneous and smaller. Thus, the abnormal growth of $TiB_2$ platelets in ceramic is effectively restrained.

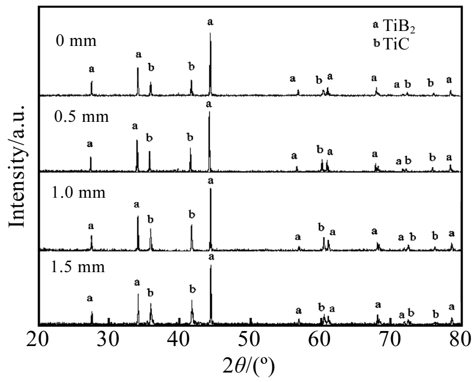


Fig.2 XRD patterns of ceramic matrix prepared by appending Ti sheet with different thickness

In terms of the thermodynamics of chemical reaction, the Ti atomic concentration at the bottom of the ceramic can be increased greatly due to the introduction of Ti sheet, and the diffusion capacity of each atomic is improved at the same time. Thus, the Gibbs free energy of the ceramic liquid becomes higher due to the presence of greater atomic disorder, and the $TiB_2$ primary platelets become more difficult to nucleate. Meanwhile, the superfluous Ti atoms between the ceramic and Ti alloy increase nucleation rate of $TiB_2$ and have a key role on composition uniformity of ceramics. Therefore, the microstructure of the ceramic matrix is refined, and the ultrafine-grained microstructure (characterized by the average thickness of $TiB_2$ platelets smaller than 1 μm) is presented at the thickness of Ti sheet amounted to 1.5 mm, as shown in Fig.3d.

## 2.2 Effects of Ti sheet insert on the interface of the graded composites

According to the results of the macrography in Fig.4, it can be concluded that there is only the microstructure transformation rather than a clear and strict joint interface between the ceramic and the Ti alloy steel. Meanwhile, the thickness of gradient interface obviously increases with the increase of the thickness of Ti sheet, whereas the thickness of heated-affected zone decreases clearly.

XRD patterns show that constituent phases and respective diffraction peak intensity of the joint with 1.5 mm Ti sheet change with the increase of the distance in the joint away from the ceramic, as shown in Fig.5. At the joint area of 0.5 mm away from the ceramic, the joint is composed of $TiB_2$, $TiC_{1-x}$ and TiB phases, as shown in Fig.5a. At the joint area of 1.0 mm away from the ceramic, the joint is composed of TiB, $TiC_{1-x}$ and Ti phases, and the diffraction peak intensity of Ti increases obviously, whereas the diffraction peak intensity of TiB somewhat decreases, as shown in Fig.5b. At the joint area of 1.5 mm away from the ceramic, there are Ti primary phases and $TiC_{1-x}$ secondary phases to be determined, and a few TiB phases are also detected, as shown in Fig.5c.

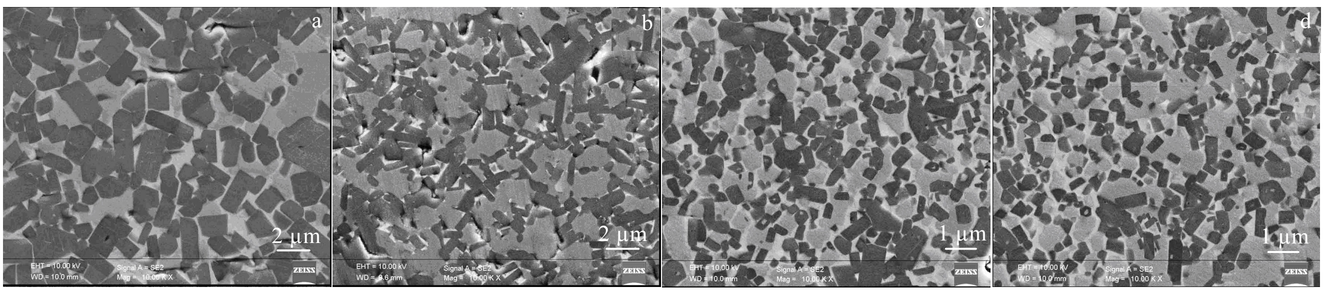


Fig.3 FESEM images of ceramic matrix prepared by appending Ti sheet with different thickness: (a) 0 mm, (b) 0.5 mm, (c) 1.0 mm, and (d) 1.5 mm

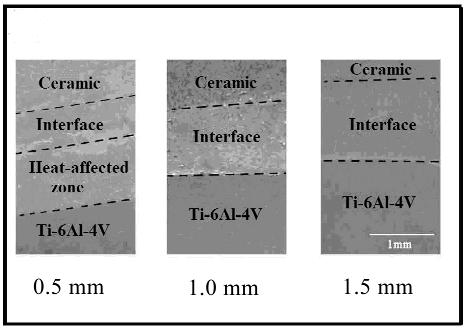


Fig.4 Macrography of the interface of $TiC-TiB_2$/Ti-6Al-4V graded composites with different thickness of Ti sheet

High-magnification FESEM and EDS results show that the microstructures of the joint are obviously refined, even ultrafine-grained microstructures characterized by an average thickness of $TiB_2$ and TiB platelets smaller than 1 μm are clearly observed, as shown in Fig.6. When it comes to the phase composition of the region far away from the ceramic, volume fraction of Ti phases becomes higher, whereas the size of $TiB_2$ and TiB platelets gradually decreases.

In term of Ref.[9], the introduction of the Ti sheet makes Ti liquid increase greatly, resulting in not only diffusion

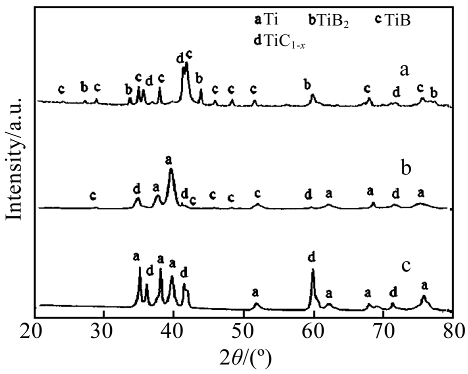


Fig.5 XRD patterns of interface of the sample with 1.5 mm Ti sheet (a-the area of 0.5 mm away from the ceramic; b-the area of 1.0 mm away from the ceramic; c-the area of 1.5 mm away from the ceramic)

toward the ceramic liquid and Ti alloy substrate but also partial consumption of heat accumulation. Ti alloy is partially molten in the presence of the achievement of full-liquid products and the rapid deposition of TiC-$TiB_2$ liquid on the surface of Ti alloy; thus, intensive atomic interdiffusion takes place between TiC-$TiB_2$ liquid and Ti alloy. As $TiB_2$ platelets are deposited completely out of the liquid ceramic at the final stage of the ceramic solidification, there are sufficient Ti atoms in residual ceramic melt due to the diffusion of Ti liquid toward liquid ceramic, so peritectic reaction between the solidified $TiB_2$ and liquid Ti has to happen in terms of B-Ti binary phase diagram[10], i.e. $TiB_2(s)+Ti(l)\rightarrow 2TiB(s)$, while the stoichiometric TiC grains continue to grow and become the non-stoichiometry $TiC_{1-x}$. As a result, $TiB_2$ platelets are refined by in situ growth of submicrometer TiB nearby $TiB_2$ platelets, resulting in the achievement of ultrafine-grained microstructures within $TiB_2$ and TiB platelets of average thickness smaller than 1 μm in the solidified ceramic nearby the joint. Meanwhile, because of the diffusion of C and B atoms toward liquid Ti, C and B atoms present a graded distribution in liquid Ti; thus, due to the participation of Ti atoms, and the more intensified peritectic reaction between $TiB_2$ solids and Ti liquid, $TiB_2$ platelets are consumed or even disappear in the joint far away from the ceramic. In addition, because of high diffusion rate of C relative to B in metallic liquid[2], there are longer diffusion distance and wider diffusion range of C than that of B in liquid Ti. Therefore, both size and volume fraction of TiB phases decrease due to the limited growth space and low atomic concentration of B.

### 2.3 Effects of Ti sheet insert on mechanical properties of the graded composites

The Vickers hardness variation from Ti alloy to ceramic was measured and compared. The results show that there is a ascending trend in Vickers hardness from Ti alloy to ceramic, as shown in Fig.7. Meanwhile, the Vickers hardness of the ceramic nearby the joint decreases with the increase of the thickness of Ti sheet. In addition, there is a descending tread in Vickers hardness gradient between the ceramic and Ti alloy with the increase of the thickness of Ti sheet.

As discussed above, free Ti atoms increase in the liquid ceramic as the thickness of Ti sheet increases. Thus, the volume and non-stoichiometry of $TiC_{1-x}$ are on the increase at the solidified stage. According to Ref.[11], the higher is the non-stoichiometry of $TiC_{1-x}$, the lower is the hardness and elastic modulus. Hence, considering the volume as well as non-stoichiometry of $TiC_{1-x}$, the ceramic nearby the joint presents a downtrend of hardness with the increase of the thickness of Ti sheet. Meanwhile, the volume fraction of TiB phases increases due to the peritectic reaction between solidified $TiB_2$ and sufficient liquid Ti. The coefficient of linear expansion of TiB is between that of $TiB_2$ and that of Ti alloy (TiB: $8.6\times10^{-6}$ $K^{-1}$, $TiB_2$: $6.4\times10^{-6}$ $K^{-1}$, TiC: $7.4\times10^{-6}$ $K^{-1}$, Ti: $9.0\times10^{-6}$ $K^{-1}$); thus, residual stress is relieved strongly at the final solidified stage. What is more, hardness of TiB is smaller than that of $TiB_2$ (TiB: 28.0 GPa, $TiB_2$: 34.0 GPa).

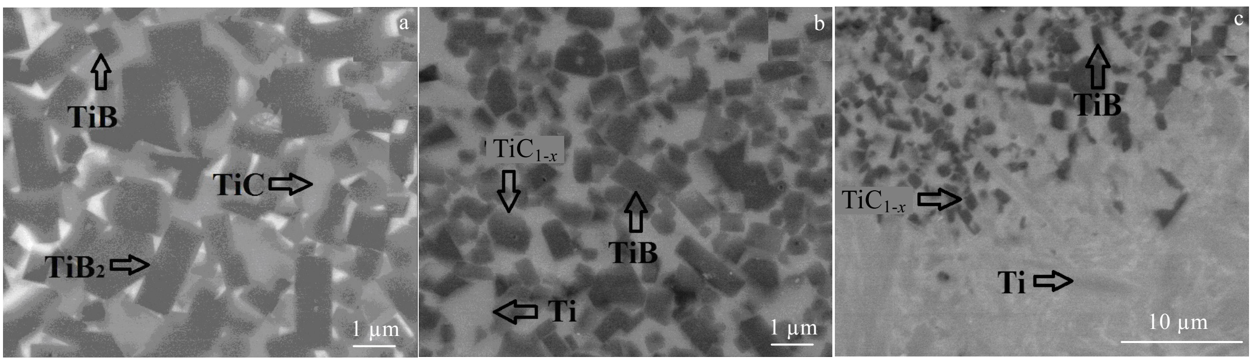


Fig.6 FESEM images of the interface with 1.5 mm Ti sheet: (a) the area of 0.5 mm away from the ceramic; (b) the area of 1.0 mm away from the ceramic; (c) the area of 1.5 mm away from the ceramic

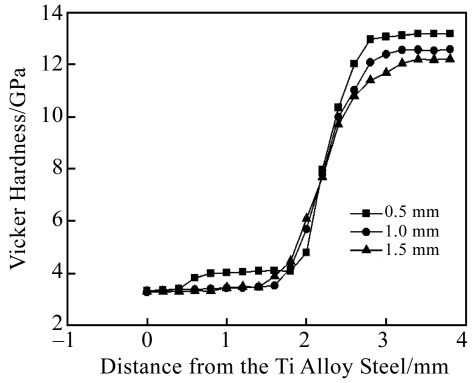


Fig.7 Vicker hardness distribution of the interface of TiC-$TiB_2$/Ti-6Al-4V composite with different thickness of Ti sheet

Therefore, the gradient of Vickers hardness decreases with the increase of the thickness of Ti sheet due to the presence of numerous TiB phases.

In addition, interlaminar shear strength of the graded composite with different thickness of Ti sheet is shown in Table 1. The results show that the shear strength increases with the increase of the thickness of Ti sheet. So it is considered that increasing thickness of Ti sheet can bring clearly the improvement in the microstructure homogeneity, thereby greatly upgrading the properties of the graded composite of $TiB_2$-based ceramic and Ti-6Al-4V steel.

FESEM images show that there is a mixed fracture mode of the intergranular fracture along $TiB_2$ platelets and TiB grains, the transgranular fracture in TiC grains and the ductile tearing in Ti alloy crystallites nearby the joint, as shown in Fig.8. High elastic modulus (meaning high strain energy release rate of $TiB_2$ during fracture) and the solidified surface of $TiB_2$ platelet (meaning mismatch incoherent interface between $TiB_2$ and the others) make its interface debonding energy far smaller than its fracture energy, thereby initiating crack deflection, crack bridging and subsequent pullout through intergranular fracture along $TiB_2$ platelets. Meanwhile, the melting heat consumption of the Ti sheet actually reduces the heat-affected zone (HAZ) of Ti alloy. In terms of Ref.[6], the solidified microstructure in HAZ of Ti alloy is the weakest part in the joint of the ceramic to Ti alloy in the presence of the coarsened column-like grains and the shrinkage. In addition, the Ti sheet insert not only releases the stress concentration between the ceramic and Ti alloy, but also refines the grain size of $TiB_2$ platelets and TiB grains. Warp this all together, the cooperative action of HAZ reducing by Ti sheet nearby Ti alloy with precipitation strengthening by micro-nanometer $TiB_2$ platelets and TiB grains in the intermediate presents the graded composite with high interlaminar shear strength.

**Table 1 Shear strength of the interface of TiC-$TiB_2$/Ti-6Al-4V graded composite with different thickness of Ti sheet**

| Thickness/mm | Shear strength/MPa |
|---|---|
| 0 | 175±25 |
| 0.5 | 192±45 |
| 1.0 | 230±30 |
| 1.5 | 316±25 |

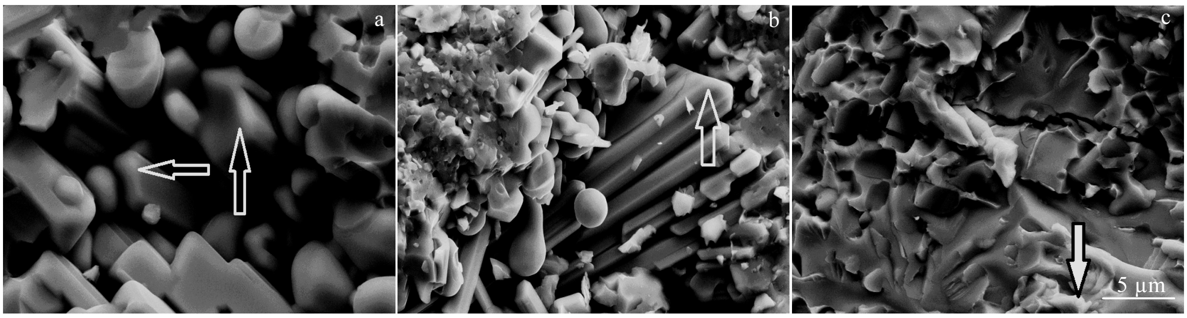


Fig.8 FESEM images nearby the interfacial region: (a) $TiB_2$ platelets pullout; (b) TiB platelets pullout; (c) ductile tearing of Ti

## 3 Conclusions

1) With the increasing of the thickness of Ti sheet, the thickness of graded interfacial region increases, and homogeneous fine-grained microstructure is achieved in the ceramic matrix nearby the interfacial region, whereas the thickness of heated-affected zone decreases clearly.

2) Because of fusion bonding and atomic interdiffusion of liquid ceramic an liquid Ti, peritectic reaction takes place, i.e. $TiB_2(s)+Ti(l)\rightarrow 2TiB(s)$, followed by direct growth of TiB solids out of Ti liquid, resulting in the rapid decrease of $TiB_2$ both in size and volume, and continuously-graded microstructure of multilevel and multiscale is finally achieved in the joint.

3) The joint presents not only a transitional change in Vickers hardness but also the high shear strength of (316±25) MPa between the ceramic and Ti alloy.

## References

1 Contreras L, Turruillas X, Vaughan G B *et al*. *Acta Materials*[J], 2004, 52: 4783

2 Vallauri D, Atlas I C, Adrian A. *Journal of European Ceramic Societies*[J], 2008, 28: 1697

3 Zhang Y, Feng D, He X. *Journal of Iron and Steel Research International*[J], 2006, 13: 1

4 Huang X G, Zhang L, Zhao Z M *et al*. *Material Science Engineering A*[J], 2012, 553: 106

5 Zhao Z M, Zhang L, Wang M Q. *Rare Metal Materials and Engineering*[J], 2013, 42(S1): 383 (in Chinese)

6 Huang X G, Zhao Z M, Zhang L. *Material Science Engineering A*[J], 2013, 564: 400

7 Zhao Z M, Zhang L, Song Y L. *Scripta Materialia*[J], 2009, 61: 282

8 Yin D J, Zhao Z M, Zhang L. *Acta Materiae Compositae Sinica*[J], 2015, 32(6): 1824 (in Chinese)

9 Wang L L, Munir Z A, Maximov Y M. *Journal of Materials Science*[J], 1993, 28: 3798

10 Dai Y N. *Binary Alloy Phase Diagrams*[M]. Beijing: Science Press, 2009 (in Chinese)

11 Vallauri D, Shcherbakov V A, Khitev A V. *Acta Materialia*[J], 2008, 56: 1388


# 中间钛片对 $TiB_2$ 基陶瓷/钛合金梯度复合材料组织及性能的影响


陈　硕, 赵忠民, 张　龙, 程兆刚, 于贵波

(陆军工程大学 特种陶瓷实验室，河北 石家庄 050003)



**摘　要：**在钛合金与陶瓷粉末之间引入厚度0.5~1.5 mm的中间钛片，采用自蔓延离心熔铸工艺快速制备出了$TiB_2$基陶瓷/钛合金梯度复合材料。经过XRD、FESEM 和 EDS分析表明，添加钛片对陶瓷相没有明显的影响，但随着中间钛片厚度的增加，不仅细化陶瓷基体并改善其组织均匀性，而且增加了梯度界面厚度，减小甚至消除了钛合金基底热影响区。同时，热真空条件下液态陶瓷与钛合金之间发生熔化连接和原子互扩散，进而在凝固后期诱发$TiB_2$与Ti液的包晶反应$TiB_2(s) + Ti(l) \rightarrow 2TiB(s)$，TiB自Ti液中的析晶反应和TiB与Ti液的共晶反应，实现了$TiB_2$的消减及TiB的生长，不仅改善了界面的残余应力，而且获得了陶瓷/钛合金多尺度多层次复合。界面组织结构的梯度演化与陶瓷/钛合金的热匹配不仅使梯度材料的硬度呈连续变化，而且使界面剪切强度达到了(316±25) MPa。



**关键词：**梯度复合；自蔓延；界面结构；原子互扩散；热匹配



作者简介：陈　硕，男，1991 年生，硕士生，陆军工程大学特种陶瓷实验室，河北 石家庄 050003，电话：0311-87994683，E-mail: 1136445516@qq.com