

# Laminated Composite with 3D-network Graded Microstructure from TiB<sub>2</sub>-based Ceramic to 42CrMo alloy Steel

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**Keywords:** laminated composite; reaction fusion; 3D-network graded microstructure

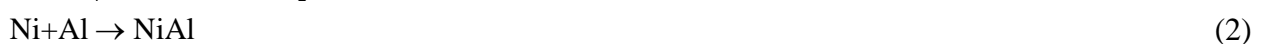
**Abstract.** Based on liquid fusion and atomic interdiffusion of TiB<sub>2</sub>-based ceramic and 42CrMo steel, the ceramic-metal laminated composites with interfacial 3D-network span-scale graded microstructures were achieved by combustion synthesis in high gravity field. The presence of respective atomic concentration gradient of Ti, B, C, Fe and the others between the ceramic and the steel reasoned for continuously-graded interfacial microstructure in which the TiB<sub>2</sub> and TiC phases transform sub-micrometer, micro-nanometer grains from the micrometer ones. The Fe-based liquid flow from the ceramic to the steel substrate resulted in the 3D-network distribution of Fe-based alloy phases from the ceramic to the steel substrate. Hence, interfacial shear fracture presented the mixed mode consisting of intercrystalline fracture along fine TiB<sub>2</sub> platelets and ductile fracture in Fe-based alloy phases, presenting interfacial shear strength  $415 \pm 25$  MPa of the laminated composite.

## Introduction

a new material concept of functionally graded materials (FGMs) has been proposed to increase adhesion and to minimize the thermal stresses in metallic-ceramic composites developed for high-temperature application [1]. At present, a series of new technologies, such as spark plasma sintering, chemical vapor deposition (CVD), plasma spraying (PS), laser cladding (LC), electric beam surface cladding (EBSC), electric beam welding (EBW) and so on, have developed to prepare ceramic-metal FGMs bulk, coating and joint, and the processing of FGMs coating in the industrial scale has reached a considerable level of maturity [2], however, because of the limits by powder forming process and heavy precision equipment, the routes of large-scale FGMs bulks and joints are still at the developing stage [3]. Hence, that actively develops a series of low-energy-consumption, low-cost and rapid-production-flow routes along with the novel processing assisted with external-field (i. e. gravitational, centrifugal, thermal, magnetic, electrical, electro-magnetic, ultrasonic and others) for preparing FGMs bulks have become an important issue of FGMs development in the world. Recently, based on reaction fusion and liquid interdiffusion, the laminated composites of TiB<sub>2</sub>-based and Ti-6Al-4V alloy with span-scale graded microstructures have been achieved by combustion synthesis in high gravity field [4-6]. Hence, by substituting 42CrMo steel for Ti-6Al-4V alloy as the metal substrate, the experiment is renewed to prepare the laminated composite of TiB<sub>2</sub>-based ceramic and 42CrMo steel, and interfacial constitution, microstructure evolution and interfacial bonding of the ceramic and the steel are discussed.

## Experimental

B<sub>4</sub>C powder of the purity larger than 98% and particle size smaller than 3.0 μm, Ti powder of the purity larger than 99% and particle size smaller than 30 μm were selected as the components of the primary system, as shown in Eq. 1. Ni and Al powder with the purity larger than 99% and particle size smaller than 30 μm were chosen to constitute the composite additive, as shown in Eq. 2. The mass ratio of Ni-Al composite additive to Ti-B<sub>4</sub>C primary system was 1:9.



After blending and mechanically activating the above powders in ball milling machine for 4h, the powder blends were pressed to be the powder compacts. Subsequently, 42CrMo steel plates of the diameter 100 mm and the thickness 6 mm were put at the bottom of the crucibles, followed by filling the powder compacts in the crucible. The crucibles were fixed in the centrifugal machine system, then, the centrifugal machine started to increase the acceleration of crucible to be about 2000. As the top of the reaction system was ignited to start thermal explosion reaction in high-gravity field, the centrifugal machine continued to run for 1 min, then, and it was stopped. As the crucibles were cooled to the ambient temperature, they were removed away from the centrifugal machine, subsequently, the samples were taken out of the crucibles. Finally, the hexagonal products of the laminated materials of TiB<sub>2</sub>-based ceramic and 42CrMo steel were obtained after the samples were worked by electric discharge machining (EDM), as shown in Fig. 1.

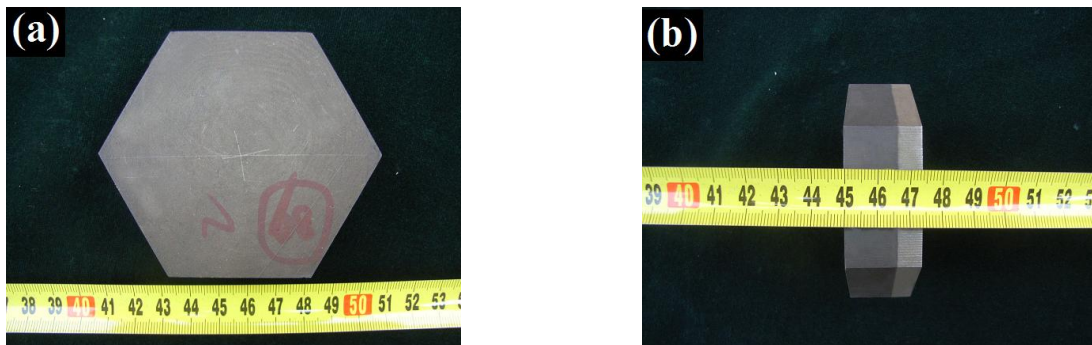


Fig. 1 Hexagonal products of the laminated composite of TiB<sub>2</sub>-based ceramics and 42CrMo steel (a) front (b) lateral

## Results and Discussion

FESEM images showed that the intermediate zone of thickness 2.0 mm was distributed at the interface between TiB<sub>2</sub>-based ceramic and 42CrMo steel substrate, presenting the microstructure transformation rather than a sharp interface from the ceramic to steel substrate, as shown in Fig. 1. XRD, FESEM and EDS results at the intermediate of near ceramic matrix and 1.0 mm away from the ceramic matrix respectively showed that the intermediate between the ceramic and the steel was composed of TiB<sub>2</sub>, TiC and Fe-based phases, as shown in Fig. 2. While TiB<sub>2</sub> and TiC both decrease sharply in size and volume fraction, the white Fe-based metallic phases increased such rapidly in size and volume fraction that sub-micrometer even micro-nanometer platelets of TiB<sub>2</sub> were obviously observed at the intermediate zone of 1.0 mm away from the ceramic, as shown in Fig. 3. Meanwhile, XRD, FESEM and EDS results at the intermediate of near steel substrate showed that a number of sub-micrometer or micro-nanometer particles of nonstoichiometric TiC<sub>1-x</sub> were embedded in the Fe-based intermediate, as shown in Fig. 4 and Fig. 5.

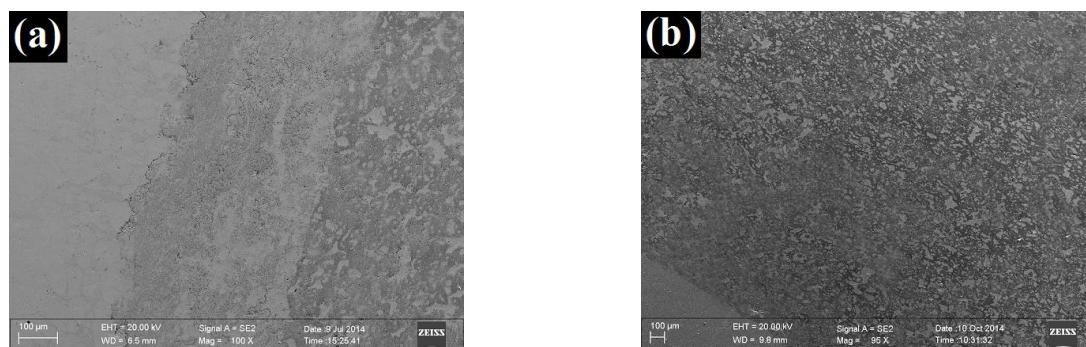


Fig. 2 FESEM images of interfacial region between TiB<sub>2</sub>-based ceramic and 42CrMo steel (a) low magnification (b) high magnification

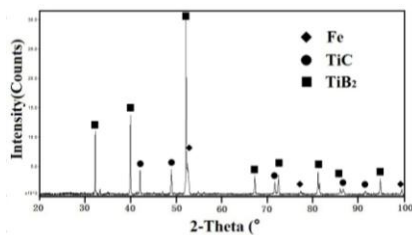


Fig. 3 XRD pattern of the intermediate of 1.0 mm away from the ceramic

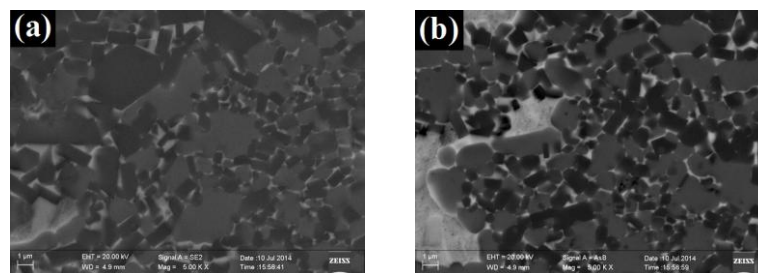


Fig. 4 FESEM images of the intermediate between the ceramic and 42CrMo substrate (a) nearby the ceramic (b) 1.0 mm away from the ceramic

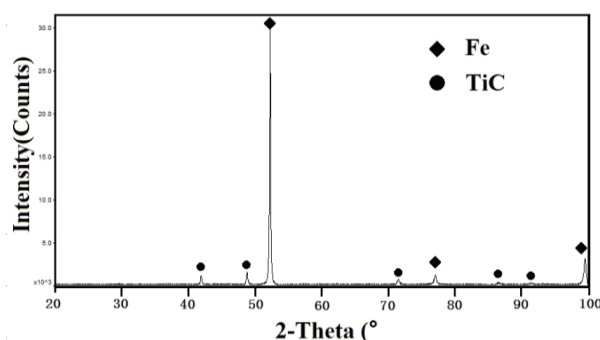


Fig. 5 XRD pattern of the intermediate nearby 42CrMo steel substrate

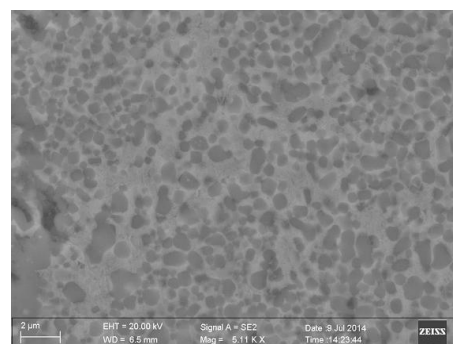


Fig. 6 FESEM images of the intermediate nearby 42CrMo steel substrate

Similar to the early stage of preparing the laminated composite of  $\text{TiB}_2$ -based ceramic and Ti-6Al-4V substrate [4-6], the introduction of high gravity field brings about the rapid deposition of liquid products toward unreacted powder compact, and promotes liquid product to infiltrate into the cavities among the powder particles, thereby presenting the enhanced heat accumulation during reaction process, so the thermal explosion mode of combustion synthesis is initiated due to the presence of high energy concentration. As a result, high-temperature liquid products consisting of  $\text{TiB}_2$ , TiC and NiAl liquids are achieved rapidly, and the surface of 42CrMo substrate is also molten, subsequently, there happens intensive liquid fusion and atomic interdiffusion between the liquid ceramic and the molten steel, resulting in the formation of the liquid intermediate from the ceramic to the steel substrate. However, different from the final stage of preparing the laminated composite of  $\text{TiB}_2$ -based ceramic and Ti-6Al-4V substrate, because of high melting entropy and high atomic concentration of Ti and B in liquid ceramic,  $\text{TiB}_2$  as the leading phases firstly nucleates and grows from the liquid ceramic nearby the intermediate, followed by the nucleation and growth of TiC. Subsequently, Fe-based liquid is extruded by the growing  $\text{TiB}_2$  and TiC solids, and constantly flows toward the the steel substrate, thus, thin Fe-based liquid remains to surround the developed  $\text{TiB}_2$  and TiC solids in the intermediate nearby the solidified ceramic, whereas the irregular coarsened Fe-based liquid has to stay at the intermediate away from the solidified ceramic. After the solidification of liquid intermediate, very thin band of Fe-based alloy is formed to surround the ceramic phases of  $\text{TiB}_2$  and TiC in the intermediate nearby the ceramic, whereas the coarse irregular particles of Fe-based alloy either alone exist or surround the  $\text{TiB}_2$  (or TiC)-enriched regions in the the intermediate away from the ceramic, respectively, as shown in Fig. 3(a) and Fig. (4). Meanwhile, because of high diffusion rate of C relative to B atoms, C atoms spread away from the liquid ceramic farther than B atoms do, there are yet some C atoms in the intermediate nearby the steel substrate even if there is absence of B atoms. As a result, there are a number of sub-micrometer or micro-nanometer particles of nonstoichiometric  $\text{TiC}_{1-x}$  embedded in Fe-based intermediate, as shown in Fig. 4 and Fig. 5. Hence, it is just liquid fusion, atomic interdiffusion and subsequent Fe-based liquid flow that 3-dimension-network spatial-span-scale (i.e.  $\text{TiB}_2$  and TiC phases transform sub-micrometer even

micro-nanometer scale from the micrometer one) graded microstructure come into existence between the ceramic and 42CrMo steel substrate.

Vickers hardness distribution from the ceramic to 42CrMo steel substrate was shown in Fig. 6. As could be seen, the change in hardness distribution between the ceramic and 42CrMo steel substrate presented the quasi-parabola relationship of the hardness to the testing distance from the ceramic to the steel substrate. Meanwhile, by using short beam shear method to measure interfacial shear strength of the ceramic and the steel, interfacial shear strength of the laminated composite measured  $415 \pm 25$  MPa as the measured values of 10 samples were averaged as the determined one. FESEM images showed that shear fracture surface of the interfaces presented a rough and uneven shape, interfacial shear fracture not only takes place at the ceramic nearby the intermediate, presenting the traces of partially-bared  $\text{TiB}_2$  platelets and the grooves resulting from pull-out and break-down of small-size  $\text{TiB}_2$  platelets, as shown in Fig. 7(a), but also happens in the intermediate, presented by large-scale ductile fracture due to the plastic deformation of Fe-based alloy. Hence, it is considered that it is just the presence of 3D-network span-scale graded microstructure between the ceramic and the steel that interfacial shear fracture presents the mixed mode of intercrystalline fracture along fine  $\text{TiB}_2$  platelets and ductile fracture in Fe-based alloy phases.

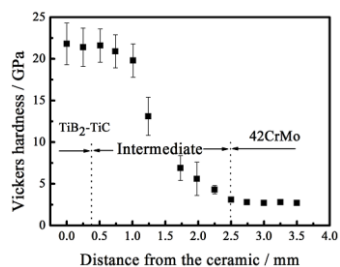


Fig. 7 Vickers hardness distribution from the ceramic to 42CrMo steel substrate

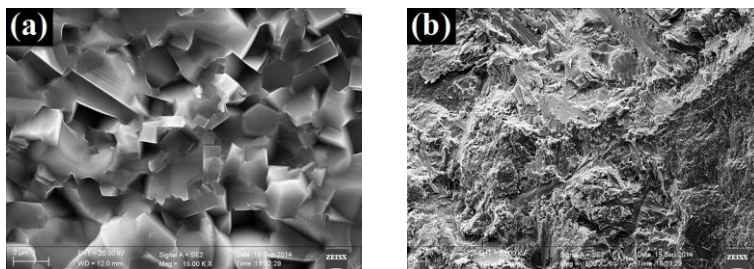


Fig. 8 FESEM fractographs of interfacial shear fracture of laminated composite of  $\text{TiB}_2$ -based ceramic and 42CrMo steel substrate

## Summary

By taking 42CrMo steel as the substrate, the laminated composites of  $\text{TiB}_2$ -based ceramic and 42CrMo steel with graded microstructure were prepared by reaction fusion and liquid diffusion during combustion synthesis in high gravity field. It was found that the laminated composite consisted of three-layer structure, i.e. the  $\text{TiB}_2$ -based ceramic, the intermediate and 42CrMo steel substrate, and the intermediate was composed of  $\text{TiB}_2$ , TiC and Fe-based phases. As the intermediate was far away from the ceramic,  $\text{TiB}_2$  and TiC in the intermediate decrease sharply while Fe-based metallic phases increased rapidly, and sub-micrometer even micro-nanometer platelets of  $\text{TiB}_2$  were obviously observed at the intermediate zone of 1.0 mm away from the ceramic. Meanwhile, a number of sub-micrometer or micro-nanometer particles of nonstoichiometric  $\text{TiC}_{1-x}$  were embedded in the Fe-based intermediate nearby the steel substrate. In terms of composite process during combustion synthesis in high gravity field, liquid fusion followed by atomic interdiffusion between the ceramic and the steel results in the formation of spatial span-scale graded microstructure from the ceramic to the steel, in other word, the presence of respective atomic concentration gradient of Ti, B, C, Fe and the others between the ceramic and the steel reasons for continuously-graded interfacial microstructure in which the  $\text{TiB}_2$  and TiC phases transform sub-micrometer, micro-nanometer grains from the micrometer ones. The 3D-network distribution of Fe-based alloy phase in the intermediate is considered as a result of the Fe-based liquid flow from the ceramic to the steel substrate. Vickers hardness distribution presented the quasi-parabola relationship of the hardness to the testing distance from the ceramic to the steel substrate, and interfacial shear strength of the laminated composite measured  $415 \pm 25$  MPa. The formation of 3D-network span-scale graded microstructure between the ceramic and the steel is considered to reason for the presence of the mixed shear fracture mode of intercrystalline fracture along fine  $\text{TiB}_2$  platelets and ductile fracture in Fe-based alloy phases.

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## References

- [1] D. K. Jha, T. Kant, R. K. Singh, A critical review of recent research on functionally graded plates, *Compos. Struct.* 96 (2013) 833-849.
- [2] J. J. Sobczak, L. Drenchev, Metallic functionally graded materials: a specific class of advanced composites, *J. Mater. Sci. Technol.* 29 (2013) 297-316.
- [3] B. Kieback, A. Neubrand, H. Riedel, Processing techniques for functionally graded materials, *Mate. Sci. Eng. A362* (2003) 81-105.
- [4] Z. Zhao, L. Zhang, M. Wang, Multiscale and multilevel composite of solidified TiB<sub>2</sub> matrix ceramic to Ti-6Al-4V achieved by reaction processing in high-gravity field, *Rare Met. Mater. Eng.* 42 (2013) 383-387.
- [5] X. Huang, Z. Zhao, L. Zhang, Fusion bonding of solidified TiC-TiB<sub>2</sub> ceramic to Ti-6Al-4V alloy achieved by combustion synthesis in high-gravity field, *Mate. Sci. Eng. A564* (2013) 400-407.
- [6] Y. Song, L. Zhang, M. Zhao, T. Ma, Layered composite of solidified TiC-TiB<sub>2</sub> ceramic to Ti-6Al-4V alloy achieved by fusion bonding, *Transaction of the China Welding Institution*, 34 (2013) 37-40.