Layered Composite of TiC-TiB₂ to Ti-6Al-4V in Graded Composition by Combustion Synthesis in High-gravity Field

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Abstract. By taking combustion synthesis to prepare solidified TiB₂ matrix ceramic in high-gravity field, the layered composite of TiC-TiB₂ ceramic to Ti-6Al-4V substrate in graded composition was achieved. XRD, FESEM and EDS results showed that the bulk full-density solidified TiC-TiB₂ composite was composed of fine TiB₂ platelets, TiC irregular grains, a few of α-Al₂O₃ inclusions and Cr alloy phases, and α'-Ti phases alternating with Ti-enriched carbides constituted the matrix of the joint in which fine TiB platelets were embedded, whereas some C, B atoms were also detected at the heat-affected zone of Ti-6Al-4V substrate. The layered composite of the solidified ceramic to Ti-6Al-4V substrate in graded composition with continuous microstructure was considered a result of fused joint and inter-diffusion between liquid ceramic and surface-molten Ti alloy, followed by TiB₂-Ti peritectic reaction and subsequent eutectic reaction in TiC-TiB-Ti ternary system.

1. Introduction
Ceramic-to-metal seals and joints are assuming increasing importance in today’s technology, and it is safe to predict that their uses will increase in the future as the advantages of ceramics as construction material are realized. While ceramics possess low density, good high temperature strength and creep resistance, their fracture toughness and thermal shock resistance are poor, limiting their use in demanding applications. Metallic materials, on the other hand, possess high fracture toughness and excellent thermal shock resistance while their poor strength-related properties at high temperature generally make them unattractive. Joining ceramics to metals, to combine inherent advantages of these two kinds of materials, has been pursued to meet the material requirements in many applications.

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Hence, various ceramic-to-metal joining techniques have been developed and improved over the past 50 years, such as mechanical joining, adhesive joining, friction joining, high energy beam welding, microwave joining, ultrasonic welding, explosive welding, reaction joining, combustion reaction joining, field-assisted bonding, brazing, diffusion bonding, transient liquid phase bonding (TLPB) and partial transient liquid phase bonding (PTLPB) and so on. Among these solid state diffusion bonding and reactive metal brazing have been explored most extensively, whereas the PTLPB with the advantages of brazing and diffusion bonding is a promising technology [1-3].

However, thermal residual stresses arising from cooling after high temperature processing, and problems due to poor chemical compatibility are barriers to the wide spread used of ceramic-metal joints. The common problem has been the large difference in thermal expansion characteristics of ceramics and metals that are of interest to structural applications. The stresses that arise after joining of many ceramic-metal combinations exceed the fracture strength of ceramic, particularly in regions close to free surface near the interface, usually resulting in either cracking of the ceramic or poor strength of the joints. As a result, functionally graded joints between ceramics and metals offer a solution to the thermal stress problem and have created wide interest recently [4, 5].

Recently, large-bulk fined-grained TiC-TiB$_2$ composites are achieved by a novel process called as combustion synthesis in high-gravity field [6, 7], combustion synthesis in high-gravity field is a new method for forming a layered composite of ceramic-metal in graded composition. In this paper, based on taking combustion synthesis in high-gravity field to prepare solidified TiC-TiB$_2$ composites, and by introducing the plates of stainless steel and Ti-6Al-4V alloy at the bottom of mixed reactive powder, the experiment is renewed to obtain the joint of the ceramic and the metal, so that a novel layered composite is achieved by joining the ceramic to the metal for the applications in the field of special engineering.

2. Experimental

Raw materials 30-63 µm in particle size were prepared from high purity (>99.9%) CrO$_3$ and Al powders, while purity (>97%) B$_4$C powder with particle size < 3 µm and high purity (>99%) Ti powder with particle size < 34 µm. The molar ratio (Ti to B$_4$C) of 3:1 was chosen as the starting composition, so the composition of the solidified TiC-TiB$_2$ composite was determined by Eq. 1. In order to obtain full-liquid reaction products in combustion reaction, the adiabatic temperature of the whole combustion system was designed as 3200°C, and the (CrO$_3$+Al) subsystem was added as the activators for increasing the adiabatic temperature according to Eq. 2. In order to protect the ceramic of TiC-TiB$_2$ liquid from the oxidation, CaF$_2$ powders (density of 3.18 g · cm$^{-3}$ and a melting temperature of 1423 °C) were used as flux and were mixed with the thermit of (CrO$_3$+Al), the mass fraction ratio of the primary system (Ti+B$_4$C+CrO$_3$+Al) to the flux-mixed system (CaF$_2$+CrO$_3$+Al) was determined as 1:1.

$$3\text{Ti}+\text{B}_4\text{C} \rightarrow \text{TiC}+2\text{TiB}_2$$  \hspace{1cm} (1)

$$\text{CrO}_3+2\text{Al} \rightarrow \text{Al}_2\text{O}_3+\text{Cr}+1094\text{kJ}$$  \hspace{1cm} (2)
After mixing the above powders, a Ti-6Al-4V alloy plates with 10 mm in thickness and 150 mm in diameter were put at the bottom of the crucibles, then, the crucibles were filled with the reactive blends of the above powders at constant pressure and inserted into two combustion chambers at the end of the rotating arms of the centrifugal machine. The whole combustion system were firstly ignited with the W wire (diameter of 0.5 mm) at the top of the reactive blends after the centrifugal machine had provided a high-gravity acceleration in the combustion chambers greater than 500g (g=9.8m·s⁻²). As the combustion chambers were cooled to ambient temperature, the centrifugal machine was stopped and the crucibles were taken out of the combustion chambers. Finally, TiC-TiB₂ ceramic of 4–5 mm in thickness on Ti-6Al-4V alloy substrate were obtained after the samples were taken out of the crucibles and Al₂O₃-CaF₂ flux layer at the top of the sample was eliminated by grinding.

3. Results and discussion

XRD results showed that the ceramic was composed of fine TiB₂, TiC, a few of Cr metallic binder and Al₂O₃ inclusions, as shown in figure 1. Hence, TiC and TiB₂ in ceramic prepared in current experiment are both close to their respective stoichiometry, which promises the achievement of stoichiometric TiC-TiB₂ by combustion synthesis in high-gravity field. FESEM images and EDS results showed a large number of randomly-orientated, fine TiB₂ platelets (presented by the dark areas in figure 2) were uniformly embedded in the irregular TiC grains (presented by the grey areas in figure 2) and Cr metallic phases (presented by the white areas in figure 2), and a few of black inclusions of α-Al₂O₃ were also observed, as shown by the arrow in figure 2. Physical and Mechanical properties showed that density, relative density, microhardness and fracture toughness of TiC-TiB₂ ceramic were 4.3 g · cm⁻³, 98.5%, 25.1 GPa and 14.5 ± 3.5 MP · m⁻⁰.⁵, respectively. Meanwhile, FESEM images of crack propagation paths showed that crack deflection and crack bridging are considered the main interaction mechanisms between the crack and TiB₂ platelets, resulting in the achievement of pull-out toughening by TiB₂ platelets, as shown by the arrow in figure 3. Thus, greater crack-opening displacement within the bridging zone is achieved, so the stress concentration around crack tip is relieved due to the presence of the closure stress behind the crack tip, resulting in greater resistance to crack propagation in the ceramic. Hence, high fracture toughness of TiC-TiB₂ ceramic results from the coupled toughening mechanisms of crack deflection, crack bridging and pull-out by TiB₂ platelets along with plastic deformation by Cr metallic binder.

![XRD patterns of the TiC-TiB₂ ceramic](image)

**Figure 1.** The XRD patterns of the TiC-TiB₂ ceramic.

According to the literature [6-8], the procedure of preparing bulk solidified TiC-TiB₂ composites by combustion synthesis in high-gravity field is described in brief as follows: by selecting (B₄C+Ti+C)
as the primary system and the thermit of (CrO$_3$+Al) as the subsystem, and designing the adiabatic temperature above the melting point of all products, combustion synthesis was conducted in the presence of a high-gravity acceleration larger than 500g, finally, near-full-density TiC-TiB$_2$ composites with fine even ultrafine microstructures were achieved through rapid solidification of liquid TiC- TiB$_2$ ceramics. Moreover, it can be concluded that the new processing for preparing the solidified TiC-TiB$_2$ composites involves three stages: formation of the immiscible liquids consisting of Ti-Cr-C-B liquid and oxide liquid following thermit reaction and the decomposition of B$_4$C during the first stage, formation of the layered melt in high-gravity field due to density difference between the immiscible liquids of Ti-Cr-C-B liquid and oxide liquid during the second stage, and formation of TiC-TiB$_2$ solidified fine even ultrafine microstructures due to rapid coupled growth of TiC and TiB$_2$ phases from Ti-Cr-C-B liquid during third stage. Hence, similar to the preparation of bulk solidified TiC-TiB$_2$ composite, the formation of the ceramic on Ti alloy substrate is a result of the rapid deposition of TiC-TiB$_2$-Cr liquid, followed by rapid solidification of the liquid ceramic on the top surface of Ti alloy substrate.

![Figure 2. FESEM microstructure of TiC-TiB$_2$ ceramic.](image1)

![Figure 3. FESEM image of crack propagation path at polished ceramic.](image2)

FESEM images showed that there was only the microstructure transformation rather than a clear joint interface between the ceramic and Ti alloy, as shown in figure 4. Meanwhile, compared with the ceramic microstructure far away from the joint, the microstructure of the ceramic nearby the joint was obviously refined, the ultrafine-grained microstructure characterized by the average thickness of fine platelets smaller than 1 μm was achieved, as shown in figure 4(b) and figure 4(c). In addition, a few of isolated Al$_2$O$_3$ inclusions were observed only at the area of the ceramic, as shown in figure 4(c).
Figure 4. FESEM images of the microstructures from TiC-TiB₂ ceramic to Ti alloy substrate. (a) joint between the ceramic and Ti alloy substrate (b) the ceramic nearby the joint (c) joint area (d) Ti alloy substrate far away from the joint

The XRD patterns and FESEM images show that the joint area was composed of martensitic Ti, TiB, TiB₂ and Ti-enriched carbides, as shown in figure 5 and figure 6. A considerable amount of ultrafine hexagonal-pillar-shaped primary TiB grains (diameter of 0.5 to 1.0 μm and length of 0.5 to 1.5 μm) and fine spherical Ti-enriched carbides are distributed in the α’-Ti martensitic matrix, what’s more, some coarse TiB₂ platelets are also obtained, as shown in figure 6.

Figure 5. The XRD patterns of the fused joint area.
Figure 6. The FESEM image of fusion-induced joint between TiC-TiB₂ ceramic and Ti alloy.

Due to the instant release of high chemical energy of combustion system in high-gravity field, the surface of Ti alloy substrate at the bottom of the liquid TiC-TiB₂ is rapidly molten, while the introduction of high-gravity field makes the energy-release rate of chemical reaction increased, and combustion rate is so rapidly increased that the combustion characterization in high-gravity field is similar to one of thermal explosion, resulting in not only rapid escape of the gas in reactive blend during combustion reaction but also the formation of thermal vacuum circumstances around the products. Subsequently, C and B atoms in liquid TiC-TiB₂ ceramic rapidly diffuse into the molten Ti alloy substrate, while Ti atoms in the molten substrate of Ti alloy simultaneously diffuse into the nearby liquid TiC-TiB₂ ceramic. As a result, at initial stage of solidification a number of TiB₂ solids as the primary phases precipitate from TiC-TiB₂ liquid, followed by peritectic reaction (TiB₂ + Ti → TiB) due to the presence of liquid Ti alloy, finally, a number of ultrafine TiB platelets (diameter of 0.5 to 1.0 μm and length of 0.5 to 1.5 μm) come to existence around the joint of ceramic to Ti alloy, resulting in the achievement of the ultrafine-grained microstructure in joint region and the ceramic nearby the joint, as shown in figure 4(b) and figure 6. Meanwhile, because of high diffusion rate of C relative to B in molten Ti alloy and the isotropy of TiC in crystallography, a number of Ti-enriched carbides develop at the joint area due to rapid growth of TiC crystals, moreover, some fine Ti-enriched carbides are also found at the area nearby the Ti solid alloy due to rapid atomic diffusion of C toward solid Ti substrate.

The high-magnification FESEM micrograph of the substrate and heat-affected zone (HAZ) of Ti-6Al-4V alloy is shown in figure 7. The Ti-6Al-4V substrate consists of equiaxed α and intergranular β phases; however, the heat-affected zone of Ti-6Al-4V substrate nearby the joint area shows the presence of a number of needle-shaped grains, as shown in figure 4(d) and figure 7. XRD and EDS results further determined that those needle-shaped grains embedded in the Ti-6Al-4V substrate were in fact α’-Ti martensites. By considering the high heat conductivity of Ti alloy substrate, a part of α-Ti phases at Ti alloy substrate away from the joint area transform into β-Ti phases once the temperature at the area is somewhat higher than transformation temperature of α→β, as a result, some needle-
shaped $\alpha'$-Ti martensites inevitably come to existence in $\alpha$-Ti matrix through martensitic transformation of $\beta \rightarrow \alpha'$ due to rapid cooling of solid Ti alloy substrate, as shown in figure 7.

![Figure 7. FESEM images of the HAZ.](image1)

![Figure 8. The dependence of the microhardness on the distance from ceramic to the Ti substrate.](image2)

The microhardness was measured from the ceramic to the substrate of Ti alloy, and the change in microhardness with the distance from the TiC-TiB$_2$ to the substrate was shown in figure 8. The maximum microhardness measured 25.1 ± 3.5 GPa at TiC-TiB$_2$, and high hardness of TiC-TiB$_2$ is considered to benefit from the achievement of fine-grained microstructure in near-full-density ceramic. The microhardness of the surface-alloyed substrate of Ti alloy measured 6.4 to 7.3 GPa, which was much lower than that of TiC-TiB$_2$ due to the presence of martensitic Ti, but presented a near-double increase over that (about 3.2 to 3.5 GPa) of Ti alloy substrate, and the phenomenon is considered to be a results of the achievement of the surface-alloyed substrate of Ti alloy containing a number of hard TiC and TiB phases.

Meanwhile, the transitional change in microhardness was observed clearly from the ceramic to Ti alloy substrate, whereas shear strength of TiC-TiB$_2$ ceramic to Ti-6Al-4V substrate measured 450 ± 35 MPa. As discussed above, the ceramic on Ti alloy substrate is achieved by fusion bonding of liquid TiC-TiB$_2$ ceramic film and molten Ti-6Al-4V substrate to induce the surface alloying of Ti-6Al-4V substrate, thus, the joint of the ceramic to Ti alloy substrate is also achieved in continuously-graded composition by atomic interdiffusion between liquid film of TiC-TiB$_2$ and molten substrate of Ti alloy, resulting in the transition change in microhardness and high shear strength between the ceramic and the substrate of Ti alloy.

Results of the interlaminal shear strength tests showed that the fusion-induced combustion synthesis bonding in high-gravity field is a feasible and economical method to obtain joints of TiC-TiB$_2$ ceramic and Ti-6Al-4V alloy with useful strengths, comparable to some of those reported method for diffusion bonded specimens prepared at significantly higher temperature.
4. Conclusion

Based on preparation of high-performance solidified TiC-TiB₂ composite by utilizing combustion synthesis in high-gravity field, a novel available process for preparing TiC-TiB₂ ceramic on the substrate of Ti-6Al-4V alloy in continuously-graded composition has been achieved. The TiC-TiB₂ ceramic was composed of a number of fine TiB₂ platelets, irregular TiC grains and a few of Cr binder and Al₂O₃ inclusions, and physical, mechanical properties showed the density, relative density, microhardness and fracture toughness of TiC-TiB₂ ceramic reached 4.3 g · cm⁻³, 98.5%, 25.1 GPa and 14.5 ± 3.5 MP · m⁰.⁵, respectively, and high fracture toughness of the ceramic benefited mainly from a coupled toughening mechanism of crack deflection, crack bridging and pull-out by fine TiB₂ platelets. XRD, FESEM and EDS results showed that there was a microstructure transformation between the ceramic and Ti alloy substrate, i.e. TiC-TiB₂ ceramic, surface-alloyed zone of Ti alloy, HAZ of Ti alloy and raw substrate of Ti-6Al-4V. Moreover, the high shear strength of 450 ± 25 MPa between TiC-TiB₂ ceramic and Ti-6Al-4V alloy was achieved.

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