

# Synthesis Mechanism of TiB<sub>2</sub>-TiC-Ni Composites Produced by Combustion Reaction of Ti-Ni-B<sub>4</sub>C System in the High-Gravity Field

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**Abstract.** TiB<sub>2</sub>-TiC-Ni composites were fabricated through combustion reaction of Ti-Ni-B<sub>4</sub>C in a high gravity field. TiB<sub>2</sub>-TiC-Ni composites were pore-free with darker TiB<sub>2</sub> phases and the brighter TiC easily distinguishable. The microstructure consisted of TiB<sub>2</sub> platelets with an aspect ratio of 2 and equiaxed TiC grains. The reaction process was controlled by the high-gravity field, which was considered to accelerate decomposition of B<sub>4</sub>C and diffusion of boron and carbon atoms. The melting Ni and Ti increased the diffusion path for boron and carbon atoms, thereby promoting the reaction process. The rapid cooling of Ti-B-C-Ni full-liquid intermediate products immediately was expected following the reaction of Ti and B<sub>4</sub>C, which was responsible for fine-grained microstructure. The microstructural investigations have confirmed the role of high gravity field and Ni dilute as promoters of densification of the final products and grain refinement in this experimental.

## 1. Introduction

Composite ceramics are of increasing interest due to their enhanced fracture resistance comparing with single-phase ceramics. Typical ceramic systems such as carbide-boride composites of transition metals are recognized as valid candidates for technological applications such as cutting tools and ceramic armour under extreme conditions due to their excellent combination of mechanical and electrical properties [1]. TiB<sub>2</sub>-TiC composites represent promising materials for wear-resistant applications such as cutting tools in comparison to conventional cermets based on WC and TiC because TiB<sub>2</sub>-TiC composites exhibit a higher hardness and chemical stability at high temperatures [2]. The available data provide evidence that the combination of good wear resistance and relatively high thermal shock and oxidation resistance renders TiB<sub>2</sub>-TiC composites an excellent candidate for cutting tools. However, no actual application of these materials is commercially available due to the fact that a cost-effective and reliable processing route allowing an accurate control of the microstructure.

Composite ceramics are usually prepared by the densification of mechanically mixed component powders [1, 2]. Since the melting temperatures of TiB<sub>2</sub> and TiC are extremely high, their fabrication to full density requires long exposures at high sintering or hot-pressing temperatures. The densification of such materials is made even more difficult due to their high degree of covalent bonding and the low self-diffusion coefficients of the constituent elements. The high processing temperatures adversely affect the microstructure due to grain growth and also lead to high production costs. As a consequence, there is an increasing need for a more practical route of fabricating bulk TiB<sub>2</sub>-TiC parts.

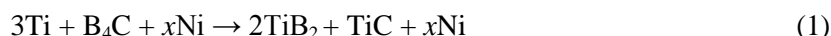
Regarding this, combustion synthesis process [3] seems to offer a promising way provided an accurate control of the process parameters. Many ceramics including TiB<sub>2</sub> and TiC can be synthesized by means of combustion synthesis. The products of the process are porous and therefore have to be compacted and generally sintered to produce bulk components suitable for engineering applications [4,



5]. Thus, the pressure on the products is usually applied to combustion synthesis process during synthesis, which could simultaneously lead to densification of monolithic and composite materials [5-9] to consolidate TiB<sub>2</sub>-TiC composites. In contrast to other combustion synthesis derivatives, this paper reported the combustion synthesis of TiB<sub>2</sub>-TiC composites in a high-gravity field which was considered to offer pressure on the TiB<sub>2</sub>-TiC. On the other hand, the addition of metal could decrease the reaction temperature by forming eutectic liquid at a lower temperature and improve the reaction rate. Among the metals, liquid Ni features low wetting angles under vacuum at 1450 °C with solid TiC and TiB<sub>2</sub>. Thus nickel was selected as the additive metal, which not only promoted the easy occurrence of combustion reaction, but also improved the abrasive and structural applications.

## 2. Experimental

The starting materials were prepared of commercial powders of Ti (99.5% purity, ~15 μm), B<sub>4</sub>C (98% purity, 3 μm) and Ni (99% purity, ~5 μm), respectively. Ti-B<sub>4</sub>C system with stoichiometric 2TiB<sub>2</sub>-TiC was chosen for the present experimental. Meanwhile, 2wt%, 4wt%, 6wt%, 8wt% Ni was added into Ti-B<sub>4</sub>C system in this experimental, respectively. Reaction formula of Ti-Ni-B<sub>4</sub>C system is as follows:



A ball milling was used to mix the above powders for 1h. The mixed powder was cold-pressed to cylindrical shape compacts of 100mm diameter, 50mm height, and 60% packing density. The compacts were loaded in a graphite crucible, which was mounted into reaction chamber of a centrifugal machine. The reaction is initiated by introducing the electrical current in a high gravity field of 1800g induced by rotating centrifugation. The centrifugal effect was directed to the reaction propagation direction. For cooling down of the sample after the reaction, the centrifugal machine continued to rotate at least for 2 min for keeping the same centrifugal effect. The reaction products were identified by X-ray diffraction (XRD, Rigaku D/max 2550PC, Japan). The density of the products was measured by the volume displacement method. Microstructure observations were carried out on polished surfaces by field emission scanning electron microscope (FESEM, Sirion200, Japan) equipped with an energy dispersive spectroscopy (EDS, LinkISIS-300, Britain). Vickers hardness was measured using a hardness tester (HVS-50, China).

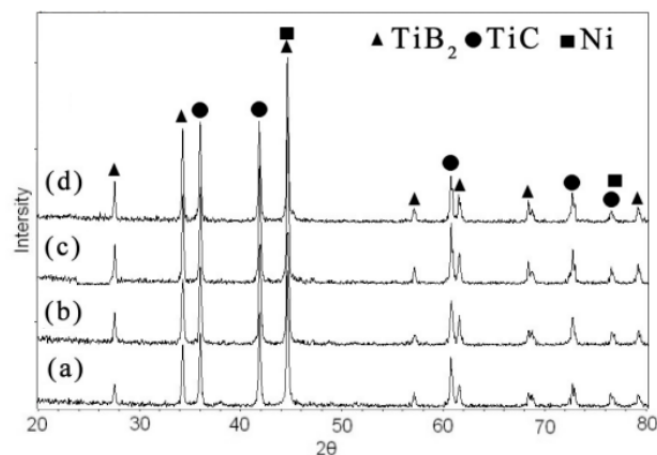
## 3. Results and discussion

XRD patterns of the as-produced ceramic materials prepared via reaction (1) with different Ni content in a high gravity field of 1800g were shown in Figure 1. TiB<sub>2</sub>, TiC and Ni phases were detected easily with no peaks indicative of unreacted Ti and B<sub>4</sub>C. It was remarked that no evidence of formation of undesired reaction products was found, such as intermetallic phases of the Ni-Ti system, transient compounds of Ti<sub>3</sub>B<sub>4</sub> or TiB and Ni-B system. Thus, full conversion of reagents into product was achieved according to reaction (1). This is also confirmed according to reaction thermodynamics that the Gibbs free energy of the reaction forming TiB<sub>2</sub> and TiC has a minimum in the system Ti-Ni-B<sub>4</sub>C. Therefore, TiB<sub>2</sub>, TiC and Ni are thermodynamically stable phase in the combustion synthesized products in the Ti-Ni-B<sub>4</sub>C system.

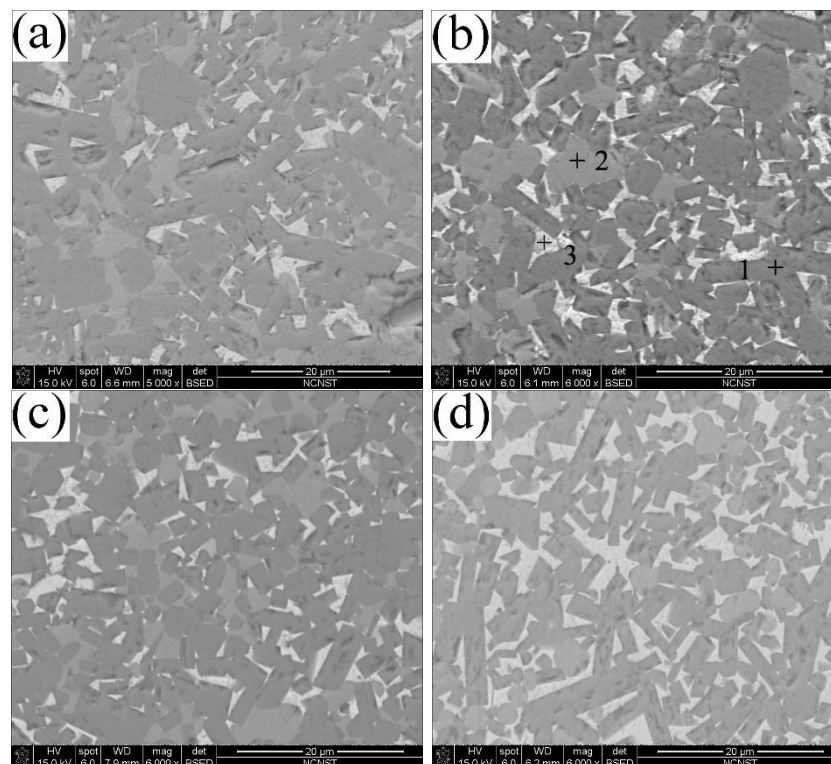
The representative microstructure of the polished cross-sections of samples produced was shown in Figure 2. By SEM observations, the darker TiB<sub>2</sub> and brighter TiC zones were easily distinguishable, as shown by the symbols +1 and +2 in Figure 2(b), respectively. The microstructure was consisted of TiC equiaxed grains and TiB<sub>2</sub> platelet grains with an aspect ratio of 2, along with white Ni phase distributed in between TiC and TiB<sub>2</sub> phases. A large number of randomly distributed fine TiB<sub>2</sub> platelets were uniformly embedded in the irregular TiC grains. In addition, the microstructural characterization revealed a significant difference in the samples with different Ni content. The difference was evident in Figure 2, as the microstructure appeared refined gradually with increasing Ni content.

The sharp edges of TiB<sub>2</sub> platelets were more distinguished easily, which confirms the formation of TiB<sub>2</sub> from solidification process. Taking the phase diagram TiB<sub>2</sub>-TiC into the account, as well as the adiabatic temperature of Ti-B<sub>4</sub>C system, it was assured that the microstructure of TiB<sub>2</sub>-TiC-x%Ni materials was characterized by solidification processing and was formed as a consequence of a

crystallization from a melt. Direct reaction between Ti and B<sub>4</sub>C to produce TiB<sub>2</sub>-TiC composites is highly exothermic, and is capable of generating temperatures exceeding the pseudo-eutectic temperature in the TiB<sub>2</sub>-TiC system of 2620 °C [10]. Ni addition serves as diluent and binder, and lead to the decrease of the combustion temperature and adiabatic temperature. To gain full liquid following the combustion reaction, no more than 8wt% Ni was added into Ti-B<sub>4</sub>C system.  $T_{ad}$  value of all Ti-Ni-B<sub>4</sub>C systems was calculated 3193 K, which was the melting point of TiB<sub>2</sub> and also exceeded the pseudo-eutectic temperature of TiB<sub>2</sub>-TiC system. Therefore, in this experimental, Ti-Ni-B-C liquid intermediate product was supposed to form after combustion reaction of Ti-Ni-B<sub>4</sub>C based on thermodynamic calculation. Meanwhile, the constitutional distribution in Ti-Ni-B-C liquid became more and more uniform due to the enhanced Stokes flow in the high gravity field of 1800g.



**Figure 1.** XRD patterns for the as-produced materials with different Ni content of (a) 2%; (b) 4%; (c) 6%; (d) 8%



**Figure 2.** FESEM images of TiB<sub>2</sub>-TiC-*x*%Ni solidified ceramics with different Ni content of (a) 2%; (b) 4%; (c) 6%; (d) 8%

According to equation (1), the super saturation of [B] in Ti-Ni-B-C liquid was much higher than one of [C], therefore  $\text{TiB}_2$  as the primary phase took lead to precipitating from Ti-B-C-Ni liquid, and grew up to form platelet due to the faceting growth behavior of  $\text{TiB}_2$  crystals. Meanwhile, following the continuous precipitation of  $\text{TiB}_2$  crystals out of Ti-Ni-B-C liquid, TiC crystals precipitated out of Ti-B-C-Ni liquid almost at the same time. TiC was characterized by the NaCl-type crystal structure, which presented the isotropy in crystal growth, thus TiC exhibited a strong tendency of high-velocity non-faceting growth. The majority of  $\text{TiB}_2$  crystals were hard to grow up due to anisotropic growth of  $\text{TiB}_2$  and also due to low diffusion velocity of [B] relative to [C]. Therefore, the achievement of fine-grained microstructure in current  $\text{TiB}_2$ -TiC-Ni composites was favored by low-velocity faceting growth of  $\text{TiB}_2$  crystals and rapid growth of TiC second phases. In addition, the presence of increasing [Ni] in the Ti-B-C-Ni liquid also increased the diffusion path length of [B] and [C] in the solidification process of  $\text{TiB}_2$  and TiC phases, which in turn also facilitated the formation of fine-grained microstructure with increasing Ni addition.

$\text{TiB}_2$ -TiC-Ni ceramics were pore-free and near fully densified. It was considered the formation of Ti-Ni-B-C liquid intermediate products was in favor for the rapid solidification and densification of  $\text{TiB}_2$ -TiC-Ni composites comparing with other combustion synthesis derivatives. Meanwhile, gas in Ti-Ni-B-C liquid intermediate products escaped more easily under the impact of gravitational force in the high-gravity field. Under the overload in the high gravity field, low-melting-point Ni was compressed into the  $\text{TiB}_2$ -TiC ceramic matrix during the solidification process. Thus, it was possible to achieve synthesis and densification simultaneously in this experimental.

#### 4. Conclusions

$\text{TiB}_2$ -TiC-Ni composites were fabricated with combustion reaction of Ti-Ni- $\text{B}_4\text{C}$  in a high gravity field of 1800g.  $\text{TiB}_2$ -TiC-Ni composites were pore-free with darker  $\text{TiB}_2$  phases and the brighter TiC easily distinguishable. The microstructure consisted of equiaxed TiC grains and  $\text{TiB}_2$  platelets with an aspect ratio of 2. The reaction process was controlled by the high gravity field and Ni dilute. High gravity field was considered to accelerate decomposition of  $\text{B}_4\text{C}$  and diffusion of boron and carbon atoms. The melting Ni and Ti offered another diffusion medium for boron and carbon atoms, thereby promoting the reaction process. Ti-B-C-Ni full-liquid intermediate products were formed following the reaction of Ti and  $\text{B}_4\text{C}$ . The rapid cooling was responsible for inherently fine-grained microstructure. The microstructural investigations have confirmed the role of high gravity field as promoter of the final products densification and grain refinement in this experimental.

#### 5. Acknowledgements

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