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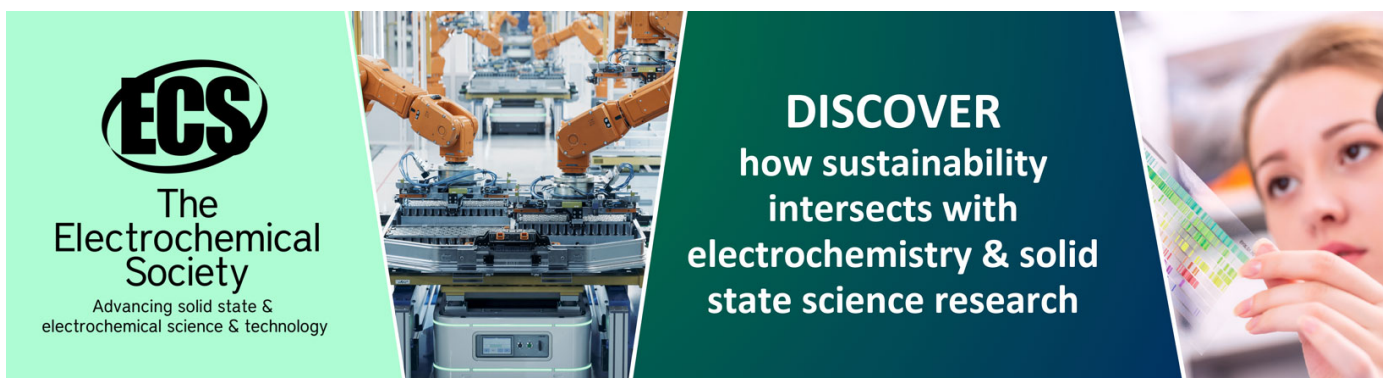
Structure formation and densification of TiB_2 -TiC-Ni composites produced by chemical reaction of Ti-B₄C system in high-gravity field

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Structure formation and densification of TiB₂-TiC-Ni composites produced by chemical reaction of Ti-B₄C system in high-gravity field

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Abstract. TiB₂-TiC-Ni composites were achieved through direct reaction of Ti and B₄C powder blends in a high gravity field of 1800 g with Ni binder. The microstructure of TiB₂-TiC composites present pore-free with darker TiB₂ platelets and the brighter TiC equiaxed grains easily distinguishable. Ti-B-C-Ni full-liquid SHS intermediate products immediately were formed following the reaction of Ti and B₄C, which was considered to yield inherently fine-grained microstructures under the rapid cooling condition. The role of high gravity field was proposed as promoter of the final products densification and grain refinement of TiB₂-TiC composites.

1. Introduction

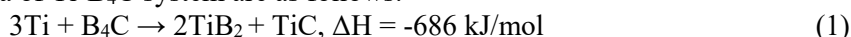
The development of ceramic composites is of increasing interest due to their enhanced fracture resistance comparing with single-phase ceramics [1]. TiB₂-TiC composites represent promising materials for wear-resistant applications such as cutting tools in comparison to conventional cermets based on WC and TiC due to their higher hardness and chemical stability at high temperatures [2]. However, actual application of these materials is limited due to the cost-effective and unreliable processing route allowing an accurate control of the microstructure. TiB₂-TiC composites could be prepared by the densification of mechanically mixed component powder of TiB₂ and TiC [1,2]. 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. Many high-melting-point ceramics including TiB₂ and TiC also were synthesized by means of SHS that was usually based on highly exothermic reactions [3,4]. Meanwhile, pressure on the products could be applied during synthesis, which lead to densification of products in the SHS process [5,6]. High pressure self-combustion synthesis (HPCS) has been used in a number of studies [7-9] to consolidate TiB₂-TiC composites.

However, with regard to TiB₂-TiC composites synthesized by SHS derivatives such as HPCS, the phase composition and microstructure of final products strongly depend on the processing parameters such as the composition and particle size of reactants, the porosity of green compacts. In contrast to other SHS derivatives, this paper reported the self-propagating high-temperature synthesis of TiB₂-TiC composites in a high-gravity field, and the structure formation and densification of the products were investigated.



2. Experimental

The starting materials were prepared of commercial powders of Ti (99.5% purity, ~15 μm), B_4C (98% purity, 3 μm) and Ni (99% purity, ~5 μm), respectively. Ti- B_4C system with stoichiometric $2\text{TiB}_2\text{-TiC}$ was chosen for the present experimental. Meanwhile, 5mol% Ni was added into Ti- B_4C system in this experimental. Reaction formula of Ti- B_4C system are 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 100 mm diameter, 50 mm height, and 60% packing density. The compacts was 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 1800 g induced by rotating centrifugation. The centrifugal effect is directed to the reaction propagation direction. For cooling down of the sample after the reaction, the centrifugal machine continues to rotate at least for 2 min keeping the same centrifugal effect. The phase composition was identified by X-ray diffraction with a step of 0.02° and a scanning rate of $2^\circ/\text{min}$. The microstructure was examined by scanning electron microscopy.

3. Results and discussion

Figure 1 showed the XRD patterns for the as-produced materials prepared via reaction (1) with a content of 5mol% Ni in a high gravity field of 1800 g. Pure TiB_2 , TiC and Ni phases were detected with no peaks indicative of unreacted Ti and B_4C or undesired intermetallic phases of the Ni-Ti system and Ti_3B_4 or TiB transient compounds. It was remarked that no evidence of formation of undesired reaction products, like, e.g. Ni-B system was found. 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_2 and TiC has a minimum in the system Ti- B_4C -Ni. Therefore, TiB_2 , TiC and Ni are thermodynamically stable phase in the SHS products in the Ti- B_4C -Ni system.

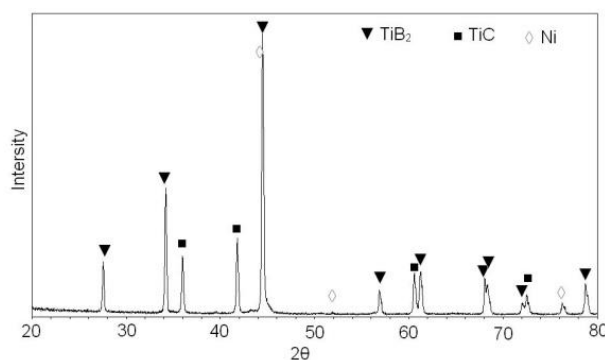


Figure 1. XRD pattern for the as-produced materials

The representative microstructure of the polished cross-sections of samples produced is shown in Figure 2. It was easily distinguishable with the brighter TiC and darker TiB_2 phases in this SEM observations. The microstructure consisted of TiC equiaxed grains and TiB_2 platelet grains with an aspect ratio of 2, along with white Ni phase distributed inbetween TiC and TiB_2 phases. In addition, the microstructural characterization revealed a significant difference between the core and the periphery of the samples. The difference is evident in Figure 2, as the microstructure appears appreciably finer at the periphery with respect to the inner core of the sample. A large number of randomly distributed fine TiB_2 platelets were uniformly embedded in the irregular TiC grains as shown in Figure 2b. This is probably due to the fact that the cooling rate in outer zone is higher due to the contact with the wall of the graphite crucible.

As the sharp edges of TiB_2 platelet were more distinguished easily, the formation of TiB_2 from solidification process are thought to be occurred in comparison with rounded shape of TiC and TiB_2

grains in TiC-TiB₂-Ni cermet synthesized by thermal explosion under pressure due to the solution/re-precipitation phenomena occurring [2]. Taking into the account the phase diagram TiB₂-TiC as well as the adiabatic temperature of Ti-B₄C system, it was assured that the microstructures of as-produced materials was characterized by solidification processing and was formed as a consequence of a crystallization from a melt.

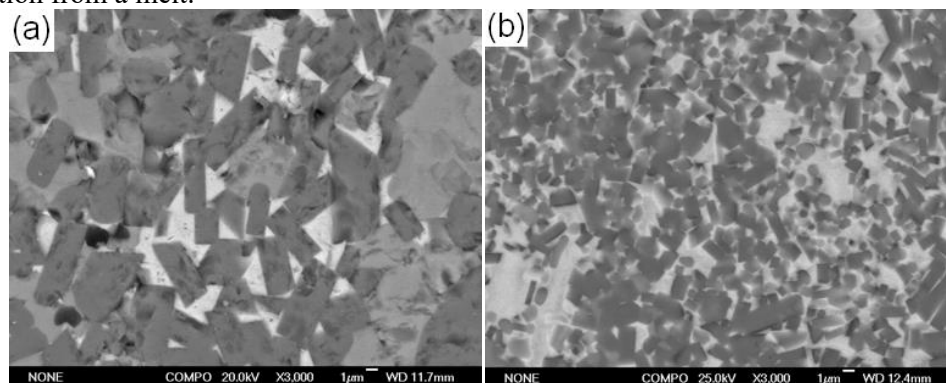


Figure 2. The microstructure in TiB₂-TiC composites:
(a) at the periphery and (b) at the inner core of the sample.

As previously mentioned, the basic principle of the SHS process deals with the high reaction heat between Ti and B₄C to generate temperatures exceeding the pseudo-eutectic temperature in the TiB₂-TiC system and gain full liquid product. According to Yang' work [10], Ti-B-C-Ni liquid was formed due to the exothermic reactions between Ti, B₄C and Ni based on their DTA results in which Ni not only served as diluent and binder, but also provided an easier route for reactant mass transfer and accelerated the occurrence of complete reaction due to the formation of Ni-Ti and Ni-B eutectic liquid. Therefore, in this experimental, Ti-B-C-Ni liquid intermediate product was also formed after SHS of Ti+B₄C+Ni based on thermodynamic calculation. Meanwhile, the constitutional distribution in Ti-B-C-Ni liquid became more and more uniform due to the enhanced Stokes flow in the high gravity field of 1800 g.

Based on solidification principle, during the solidification process of high-temperature Ti-B-C-Ni liquid intermediate product, [Ti] reacted with [B] and [C] in the Ti-B-C-Ni liquid to form TiB₂ and TiC due to their high melting point. Meanwhile, according to thermodynamic calculation, the standard Gibbs free energy of [Ti]+[B]→TiB₂ and [Ti]+[C]→TiC is far more negative relative to [Ti]+[Ni]→TiNi, [Ti]+[B]→TiB and [Ti]+[B]→Ti₃B₄. Therefore, it was concluded that TiB₂ and TiC is more easier to form than TiNi, TiB and Ti₃B₄. In this case, TiNi, Ti₃B₄ or TiB were not present in the final products as conformed by XRD results.

According to equation (1), the supersaturation of [B] in Ti-B-C-Ni liquid is much higher than one of [C] at the initial stage of solidification, therefore TiB₂ 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 TiB₂ crystals. Meanwhile, following the continuous precipitation of TiB₂ crystals out of Ti-B-C-Ni liquid, TiC crystals precipitated out of Ti-B-C-Ni liquid almost at the same time. However, since TiC was characterized by the NaCl-type crystal structure, which presented the isotropy in crystal growth, TiC exhibited a strong tendency of high-velocity non-faceting growth. The majority of TiB₂ crystals were hard to grow up due to anisotropic growth of TiB₂ and also due to low diffusion velocity of [B] relative to [C] [13]. Therefore, the achievement of fine-grained microstructures in current TiB₂-TiC composites was favored by low-velocity faceting growth of TiB₂ crystals and rapid growth of TiC second phases. In addition, the presence of [Ni] in the Ti-B-C-Ni liquid also increased the diffusion path length of [B] and [C] in the solidification process of TiB₂ and TiC phases, which in turn also facilitated the formation of fine-grained microstructure. The retainment of fine grains was possible thanks to high gravity field that will accelerate transmission of energy, mass and motion of the combustion process.

The as-produced sample was pore-free and near fully densified. It was considered the formation of Ti-B-C-Ni liquid phase transient products after SHS was in favor for the rapid solidification and densification of TiB₂-TiC composites comparing with other SHS derivatives. As SHS process is conducted in a high gravity field, gas in the liquid SHS intermediate products escape due to their mutual insolubility and difference in specific weights under the impact of gravitational force. Meanwhile, the application of the high gravity field gave rise to a compression effect which tended to limit the expulsion of gases and solid materials. Under the overlord in the high gravity field, the reacting sample was more compressed thus enhancing continuity among solidified crystals during the solidification process. The same compression through centrifugal action shrunk the sample as the reaction proceeds. Thus, it is possible to achieve synthesis and densification simultaneously.

4. Conclusions

Bulk TiB₂-TiC ceramic materials based on Ti-B₄C-Ni system have been produced through SHS in the high gravity field of 1800 g. The microstructure consisted of a number of TiB₂ platelets with an aspect ratio of 2 and average size smaller than 1 μm. Meanwhile, equiaxed TiC grains and Ni binder were distributed inbetween TiB₂ platelets. Full liquid phase SHS intermediate products consisted of Ti-B-C-Ni was considered to form immediately following the reaction of Ti-B₄C-Ni system based on the thermodynamic calculation, which allowed a solidification process. The rapid cooling of Ti-B-C-Ni was considered to yield inherently fine-grained microstructures. The application of the high gravity field give rise to a compression effect which tends to limit the gases and solid materials. Thus, it is possible to achieve synthesis and densification simultaneously.

Acknowledgements

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