Surfactant Effect on the Synthesis of $B_4C$-nano TiB$_2$ Composite by Co-precipitation Method

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Abstract
Titanium diboride is one of the candidate materials for high temperature applications and also for control rod elements in high temperature reactors. This paper presents the experimental data on the composites of $B_4C$-nano TiB$_2$ that were synthesized successfully by co-precipitation method at 1523K. Titanium tetraisopropanol, boron carbide, isopropanol and triton x-100 were used as the precursor materials. Titanium tetraisopropanol and boron carbide were dissolved in isopropanol (solution A). Then, boron carbide was dissolved in deionized water and isopropanol (solution B). Solution B was gradually added to solution A. The prepared mixture was stirred and heated at 298K for 4h. In this research, $B_4C$-nano TiB$_2$ composites are contained 10 w% TiB$_2$. The phase constitution and microstructure of $B_4C$-nano TiB$_2$ during synthesis were investigated. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to determine phase and microstructure of TiB$_2$-$B_4C$ composites. The distribution sizes of TiB$_2$ nanoparticles on $B_4C$ were calculated between 10-82 and 20-35 nm without and with surfactant, respectively.

Key words: $B_4C$-nano TiB$_2$, Surfactant, Morphology, XRD.

Introduction
As one of the hardest materials known, boron carbide ranks third behind diamond and cubic boron nitride. Boron carbide ($B_4C$) ceramics possesses excellent mechanical and physical properties of good impact and wears resistance, hardness and high melting, excellent resistance to chemical materials as well as high capability for neutron absorption [1-6]. Moreover the low density of $B_4C$ and its high Young’s modulus recommend this material for the construction of light-weight armor such as in the helicopter and similar aero-application [7]. However, the widespread application of $B_4C$ ceramics has been restricted because of the poor sinterability due to a low
self-diffusion coefficient and the low fracture toughness (< 2.2 MPa m$^{1/2}$) [8, 9].

Recently studies, some researches of $B_4C$ based-composites such as $B_4C/ZrB_2$, $TiB_2$-$TiC/Fe$, $Al_2O_3/TiB_2$, $TiB_2$-$TiC$, $B_4C/TiC$ and $B_4C/CrB_2$ have been carried out [10, 11]. It has been considered that the additions of secondary phases to $B_4C$ matrix can improve its mechanical properties [12]. Since both $TiB_2$ and $B_4C$ have high hardness and high melting points as well as chemical stability at elevated temperature, the $TiB_2$-$B_4C$ composites were expected to be used for advanced structural materials. Numerous researchers have shown the addition of $TiB_2$ to $B_4C$ can decrease the porosity level and improve the fracture toughness as well as flexural strength [13-15]. A recent study showed that hot pressing and pulsed electric current sintering aided in increasing the density of titanium diboride while decreasing the sintering time [16]. There are several methods to synthesize $TiB_2$-$B_4C$ composites. One of them to make $TiB_2$-$B_4C$ composites is via in situ reaction of $TiO_2$, carbon and $B_4C$ [17-19] or from elemental powders [20]. Another way to prepare $TiB_2$-$B_4C$ composites with up to 30 %v $TiB_2$ were made by in situ synthesis from $B_4C$, $TiO_2$ and carbon black powder mixture during densification by pulsed electric current sintering [21]. Also, the synthesis of these composites from a mixture of elements is an extremely exothermic process and combustion like methods can be employed as a practical means for their production.

For instance, $TiB_2$ can be prepared by self-propagating high-temperature synthesis (SHS) [22-25]. Mechanochemical processes referred to as mechanically induced self-sustaining reaction are similar to thermally ignited SHS methods [26].

In the present study, $B_4C$-nano $TiB_2$ composites with 10 % w $TiB_2$ were obtained by in situ synthesis from boron carbide, titanium tetraisopropanol and isopropanol. The effect of surfactant on the sizes, morphology and phases were discussed. Titanium diboride was synthesized by co-precipitation method.

**Experimental**

Bore carbide (95% pure, $B_4C$, Merck), titanium tetraisopropoxide (97%, TTIP, Alfa Aesar), isopropanol (99.6%, Merck) and triton x-100 (99% Merck) were used to synthesis the solid solution. All materials were used without further purification. Bore carbide contains 5 w% phenolic resin which used as carbon source. Deionized water was used for all experiments. The $B_4C$ powders were 1 µm for the mean size. The precursor powders were obtained by using co-precipitation method. $TiB_2$ was prepared by the reaction given below:

\[ 2TiO_2 + B_4C + 3C \rightarrow 2TiB_2 + 4CO \] (1)

Titanium tetraisopropanol (1.15 mol) and boron carbide (18.1 mol) were dissolved in isopropanol (solution A). Also, boron carbide
and triton x-100 (0.5 w%) was dissolved in deionized water and isopropanol (solution B). Solution B was gradually added to solution A. The prepared mixture was stirred and heated at 298K for 4h. In this work, B$_4$C-nano TiB$_2$ composites are contained 10 w% TiB$_2$ with and without surfactant. The mixture was placed at 423-433K till isopropanol evaporate. The X-ray diffraction pattern (XRD, X’Pert MPD, Philips, Holand) and Scanning Electron Microscopy image (SEM, XL-30 Philips, Holand) of initial B$_4$C is shown in Figures 1 and 2, respectively. The crystalline phases during the reaction were investigated by a X-ray diffractometer using Cu- k$_\alpha$ radiation (40 KV, 40 mA). The mixture of TTIP, B$_4$C and isopropanol was placed at 423-433K till isopropanol evaporate.

![Figure 1. XRD pattern of B$_4$C initial powder.](image1)

![Figure 2. SEM image of B$_4$C initial powder.](image2)
Then, the powders were milled and after that, the XRD pattern and SEM was used to determine of particles size and to study of morphology that are illustrated in Figures 3 and 4 without surfactant and Figures 5 and 6 with surfactant, respectively. These powders were heated at 1523K with 150 sccm (denotes cubic centimeter per minute at STP) argon flow. In this temperature, Ti(OH)$_4$ was changed to TiB$_2$.

![XRD pattern](image1.png)  
**Figure 3.** XRD pattern of composites at 1523 K without surfactant.

![SEM image](image2.png)  
**Figure 4.** SEM image of composites at 1523 K without surfactant.
Results and discussion

The JCPDS cards matching the spectra are 84-1286 for anatase TiO₂, 86-1129 for rhombohedra B₄C, 85-2083 for hexagonal TiB₂ and 73-2158 for H₃BO₃. Since the C source from resin is amorphous carbon, only TiO₂ and B₄C powder were found in the starting powder after calcination. Figure 1 shows the XRD pattern of initial B₄C. It is considered that a small amount of boric acid exist because of oxidation of B₄C in presence of air. The XRD patterns of calcination powders (TiB₂ phase in 10.0 w%) and the fractured and ground surfaces of the B₄C-TiB₂ composites at 1523K is shown in Figures 3 and 5 without and with surfactant, respectively.

Figure 5. XRD pattern of mixture of TTIP and B₄C after evaporation of isopropanol with surfactant.

Figure 6. SEM image of mixture of TTIP and B₄C after evaporation of isopropanol with surfactant.
Also, Figures 4 and 6 show SEM images of the B4C-TiB2 composites at 1523K without and with surfactant, respectively. B4C and TiO2 phases were identified in the calcination powders. Ti(OH)4 phase could be formed as an intermediate phase during the heating process that Ti(OH)4 almost converted into TiO2 phase. In TiB2 10 w% in situ synthesized TiB2 and B4C phases were detected in composite powder at 1523K as shown in Figures 3 and 5 without and with surfactant, respectively. Most of the TiO2 converted into TiB2 phase at this calcination temperature. Also, it is considered that longer holding time or higher pre-sintering temperature might be considered to decrease the amount of the remained TiO2 at 1523K. Study on SEM images show that the large dark gray phases were B4C and the small bright white nanoparticles were TiB2 as shown in Figures 4 and 6 without and with surfactant, respectively. The distribution sizes of TiB2 nanoparticles on B4C were calculated between 10-82 and 20-35 nm without and with surfactant, respectively.

**Conclusion**

Titanium diboride was synthesized successfully without and with surfactant by co-precipitation method using TTIP, B4C, triton x-100 and isopropanol. In this research, calcination temperature was kept for 90 minutes at 1523K. The XRD and SEM results are proved which two phases of B4C and TiB2 in both composites are identified. The distribution nanoparticle sizes of the synthesized TiB2 on surface of B4C microstructures were found between 10-82 and 20-35 nm without and with surfactant, respectively. Therefor, the distribution sizes of TiB2 nanoparticles on B4C with surfactant have been limited.

**References**