Journal of Applied Chemical Research, 10, 4, 7-13 (2016)

Journal of Applied Chemical Research
www.jacr.kiau.ac.ir

Surfactant Effect on the Synthesis of B_4C-nano TiB_2 Composite by Co-precipitation Method

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(Received 24 May 2016; Final version received 12 Jul. 2016)

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 methodat 1523K. Titanium tetraisopropanol, boron carbide, isopropanol and triton x-100were 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 TiB2, Surfactant, Morphology, XRD.*

Introduction

As one of the hardest materials known, boron carbide ranks third behind diamond and cubic boron nitride. Boron carbide (B4C) 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

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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 B4C powders were 1 μm for the mean size. The precursor powders were obtained by using co-precipitation method. TiB2 was prepared by the reaction given below:

$$2TiO_2 + B_4C + 3C \longrightarrow 2TiB_2 + 4CO \quad (1)$$

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_4C-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_4C is shown in Figures 1 and 2, respectively. The crystalline phases during the reaction were investigated by a X-ray diffractometer using Cu-k_α radiation (40 KV, 40 mA). The mixture of TTIP, B_4C and isopropanol was placed at 423-433K till isopropanol evaporate.

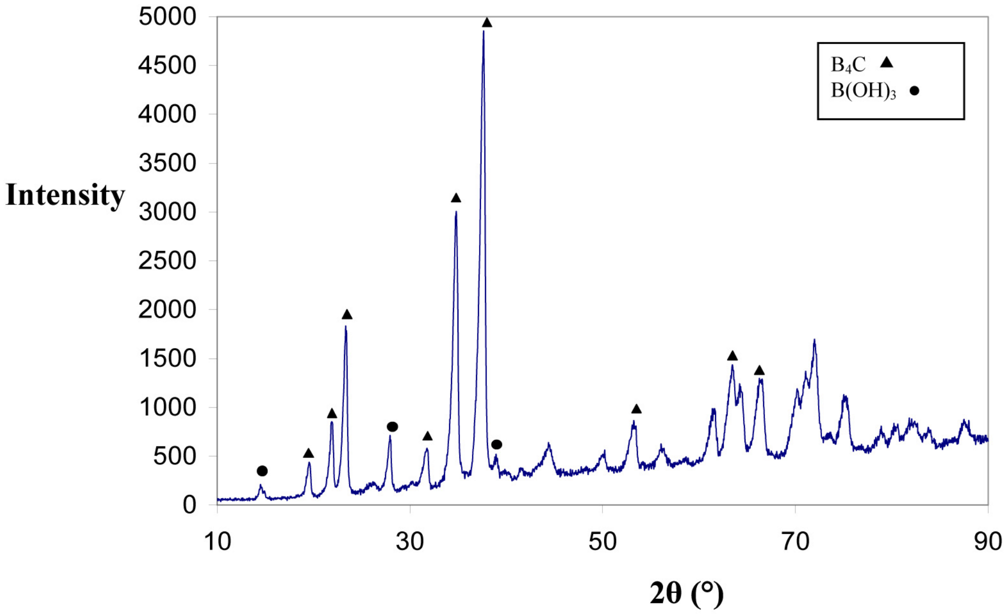

Figure 1. XRD pattern of B_4C initial powder.

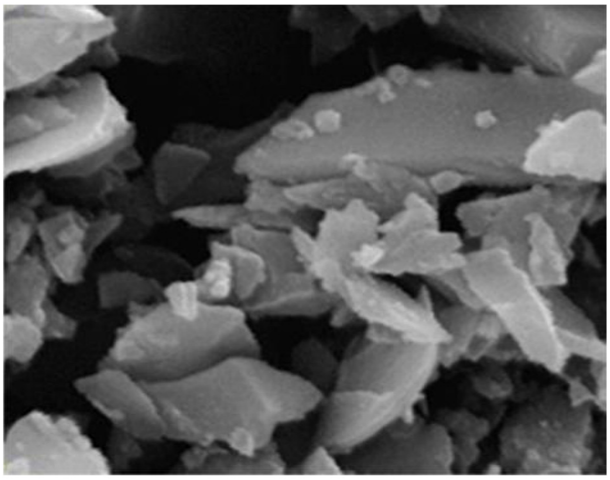

Figure 2. SEM image of B_4C initial powder.

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.

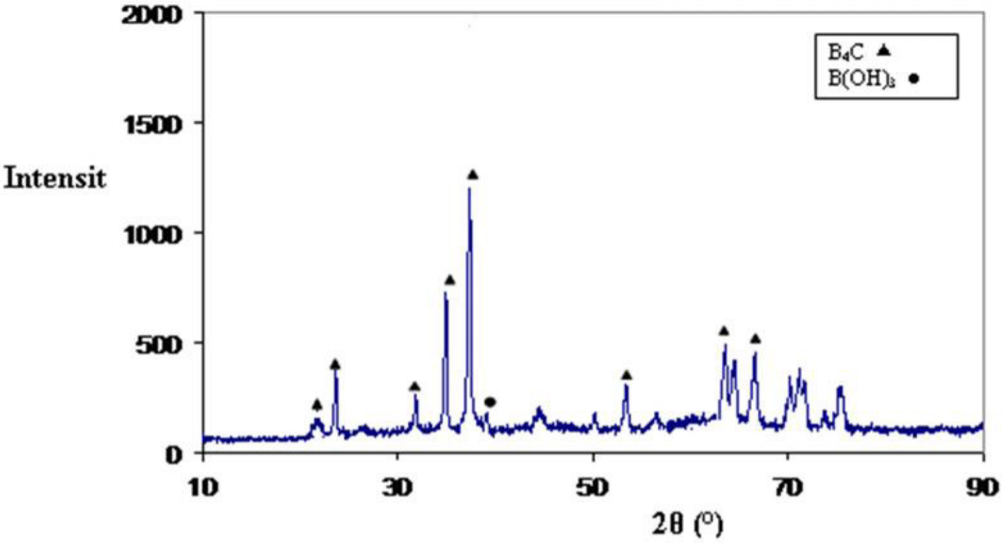

Figure 3. XRD pattern of composies at 1523 K without surfactant.

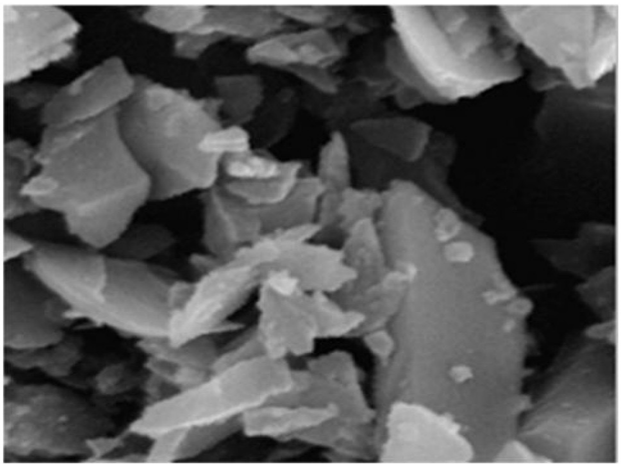

Figure 4. SEM image of composites at 1523 K without surfactant.

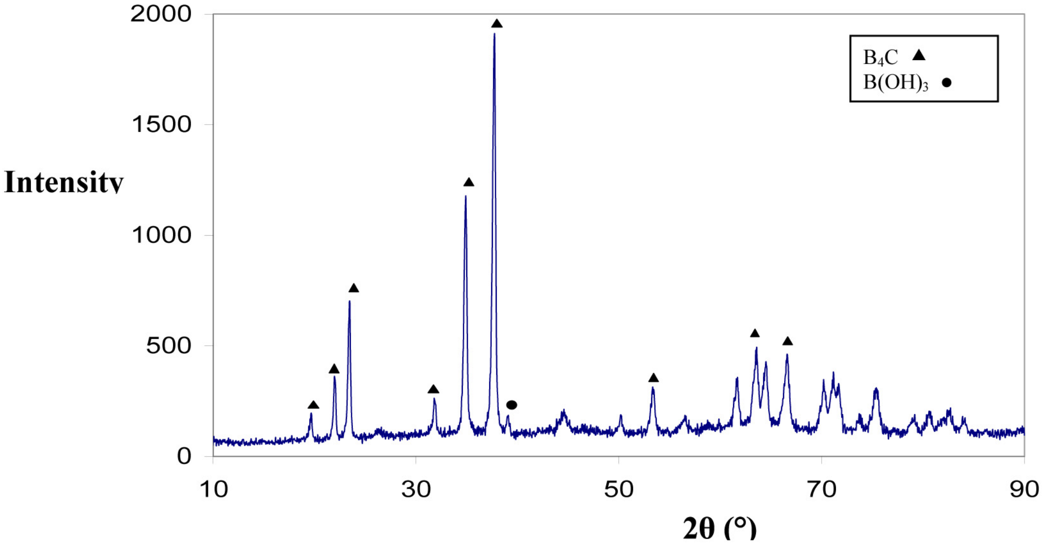

Figure 5. XRD pattern of mixture of TTIP and B_4C after evaporation of isopropanol with surfactant.

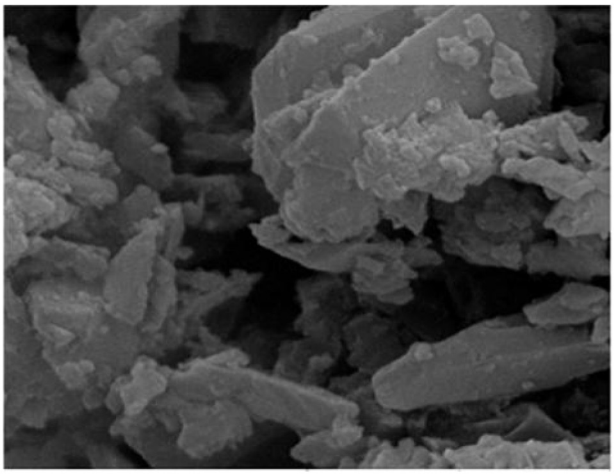

Figure 6. SEM image of mixture of TTIP and B_4C after evaporation of isopropanol with surfactant.

Results and discussion

The JCPDS cards matching the spectra are 84-1286 for anatase TiO_2, 86-1129 for rhombohedra B_4C, 85-2083 for hexagonal TiB_2 and 73-2158 for $H3BO_3$. Since the C source from resin is amorphous carbon, only TiO_2 and B_4C powder were found in the starting powder after calcination. Figure 1 shows the XRD pattern of initial B_4C. It is considered that a small amount of boric acid exist because of oxidation of B_4C in presence of air. The XRD patterns of calcination powders (TiB_2 phase in 10.0 w%) and the fractured and ground surfaces of the $B4C$-TiB_2 composites at 1523K is shown in Figures 3 and 5 without and with surfactant, respectively.

Also, Figures 4 and 6 show SEM images of the B4C-TiB_2 composites at 1523K without and with surfactant, respectively. B_4C and TiO_2 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 TiO_2 phase. In TiB_2 10 w% in situ synthesized TiB_2 and B_4C phases were detected in composite powder at 1523K as shown in Figures 3 and 5 without and with surfactant, respectively. Most of the TiO_2 converted into TiB_2 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 TiO_2 at 1523K.Study on SEM images show that the large dark gray phases were B_4C and the small bright white nanoparticles were TiB_2 as shown in Figures 4 and 6 without and with surfactant, respectively. The distribution sizes of TiB_2 nanoparticles on B_4C 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-precipitat method using TTIP, B_4C, 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 B_4C and TiB_2 in both composites are identified. The distribution nanoparticle sizes of the synthesized TiB_2 on surface of B_4C microstructures were found between 10-82 and 20-35 nm without and with surfactant, respectively. There for, the distribution sizes of TiB_2 nanoparticles on B_4C with surfactant have been limited.

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