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Temperature calcination effect on phase and morphology of B_4C-nano TiB_2 composites by co-precipitation method

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ABSTRACT

In this study, determination of titanium tetraisopropanol (TTIP) concentration and calcination temperature were used to synthesis of B_4C-nano TiB_2 by co-precipitation method. TTIP, boron carbide and isopropanol were used as the precursor materials. B_4C composites with 2.5, 5.0, 7.5, 10.0, 20.0 and 40.0 ww% TiB_2 were obtained. The ww% TiB_2 on the phase constitution and microstructure during synthesis and densification was determined. In this process, TiO_2 nanoparticles is initially converted to titanium tetrahydroxide and $Ti(OH)_4$ as intermediate product in above 1523 K for 25-65 minutes. X-ray diffraction (XRD), scanning electron microscopy (SEM) and field emission scanning electron microscopy were used to determined phase and microstructure of B_4C-nano TiB_2 composites. The distribution sizes of TiB_2 nanoparticles on B_4C were calculated between 10-40 nm. © 2015 Trade Science Inc. - INDIA

KEYWORDS

Titanium diboride;
Co-precipitation method;
Boron carbide;
Nanoparticles;
X-ray diffraction.

INTRODUCTION

As one of the hardest materials known, boron carbide ranks third behind diamond and cubic boron nitride. Being intrinsically brittle, B_4C often requires different additives to improve its sintering chemical, physical and mechanical properties. Also, diborides of group IVB transition metals are useful compounds for the high hardness and strencgth technological application at high temperature, electrical and good thermal conductivities, chemical inertness, oxidation and wear resistance, high thermal stability, high melting point (3253K), despite its low density (4.495 gcm^{-3}) and high young's modulus (524 GPa)[1]. These transition metal diborides are potential candidates for the development of materials that can withstand ultra-high temperatures and extreme environments[2].

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[3,4]. It has been considered that the additions of secondary phases to B_4C matrix can improve its mechanical properties[5]. 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

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toughness as well as flexural strength[6-8]. 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[9]. 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[10-12] or from elemental powders[13]. Another way to prepare TiB_2-B_4C composites with up to 30 vol% 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[14]. 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)[15-18]. Mechanochemical processes refered to as mechanically induced self-sustaining reaction are similar to thermally ignited SHS methods[19].

In the present research, TiB_2-B_4C composites with 2.5 to 40.0 ww% TiB_2 were obtained by in situ synthesis from bore carbide, titanium tetraisopropanol, isopropanol and resin as carbon source by using co-precipitation method.

EXPERIMENTAL MATERIALS AND METHODS

Bore carbide (95% pure, B_4C, Merck), titanium tetraisopropoxide (97%, TTIP, Alfa Aesar) and isopropanol (99.6%, Merck) were used to synthesis the solid solution. All materials were used without further purification. Bore carbide contains 5.0 ww% 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 1-3 reactions:

$$Ti[OCH(CH_3)_2]_4 + 4\ H_2O \rightarrow Ti(OH)_4 + 4\ C_3H_7OH \quad (1)$$

$$Ti(OH)_4 \rightarrow TiO_2 + 2H_2O \quad (2)$$

$$TiO_2 + 0.5\ B_4C + 1.5\ C \rightarrow TiB_2 + 2\ CO \quad (3)$$

Titanium tetraisopropoxide (99.5-2202.6g, 0.35-7.75 mol) and bore carbide (1000.01g, 18.1 mol) were dissolved in isopropanol (solution A). Also, bore carbide were dissolved in deionized water and isopropanol (solution B).

Solution B was gradually added to solution A. The obtained mixture was stirred and heated at 298 K for 4 h. In this research, B_4C-TiB_2 composites are contained 2.5-40.0 ww% TiB_2 nanoparticles. The amount of materials is given in TABLE 1.

The mixture was placed at 423-433 K till isopropanol evaporate. The X-ray diffraction pattern (XRD, X'Pert MPD, Philips, Holand) and Scannind 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 423-433 K till isopropanol evaporate.

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, respectively. This powder were heated at 1523 K with 150 sccm (denotes cubic centimeter per minute at STP) argon flow. In this temperature, $Ti(OH)_4$ was changed to TiB_2. The nanostructure and composition of the B_4C-TiB_2 composites were examined by SEM.

XRD patterns and SEM images of this change

TABLE 1 : Calculation of stoichiometric of materials

Sample	Initial B_4C (mole)	Initial TTIP (mole)	Final TiB_2 wt%	Final B_4C wt%
B_1	0.181	0.0035	2.5	97.5
B_2	0.181	0.0074	5	45
B_3	0.181	0.0113	7.5	92.5
B_4	0.181	0.0115	10.0	90.0
B_5	0.181	0.0310	20.0	80.0
B_6	0.181	0.0775	40.0	60.0

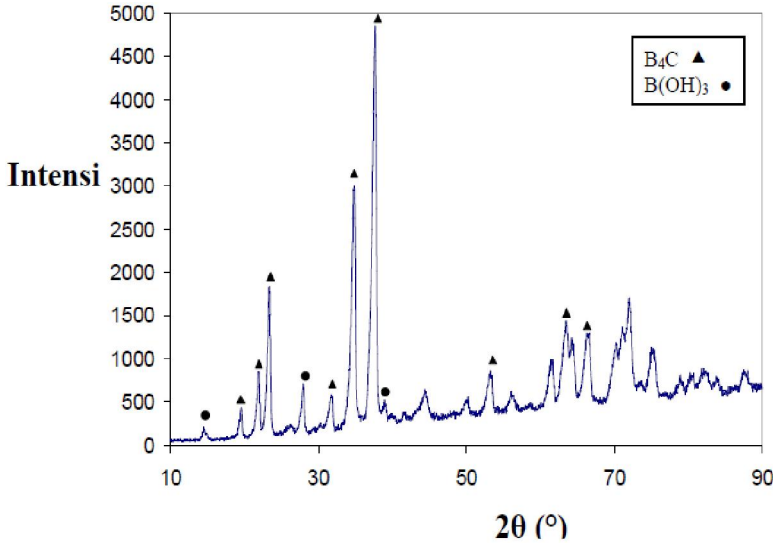

Figure 1 : XRD pattern of B_4C initial powder

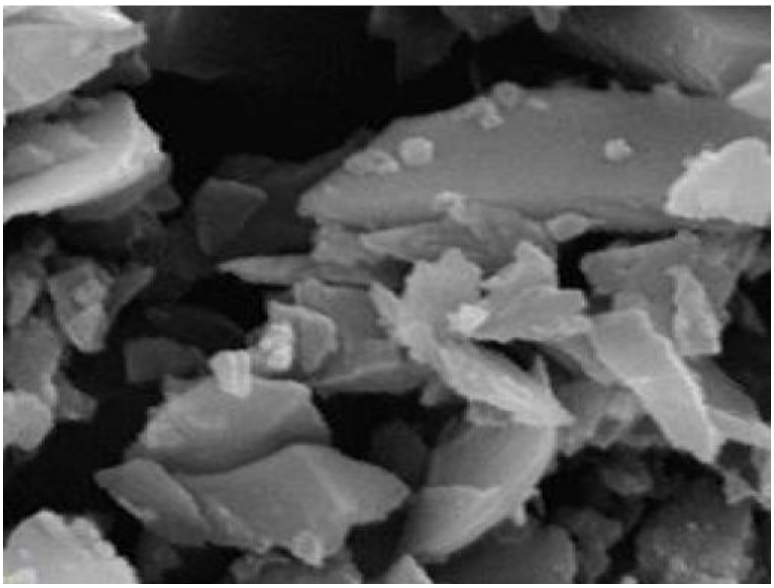

Figure 2 : SEM images of B_4C initial powder

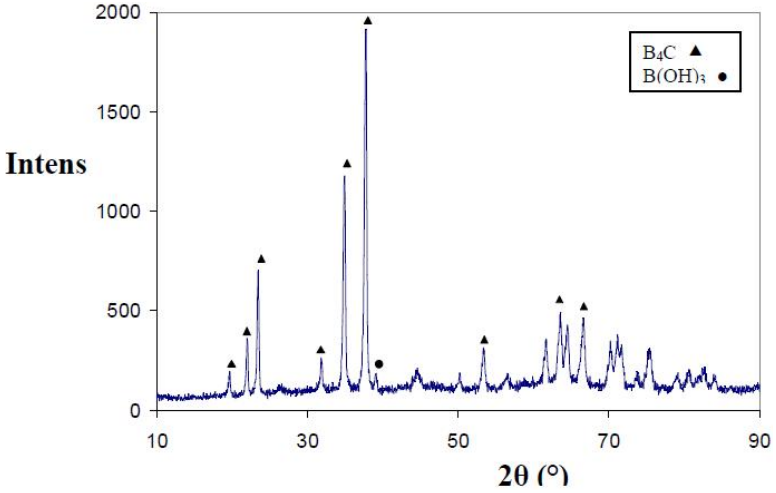

Figure 3 : XRD pattern of mixture of TTIP and B_4C after evaporation of isopropanol

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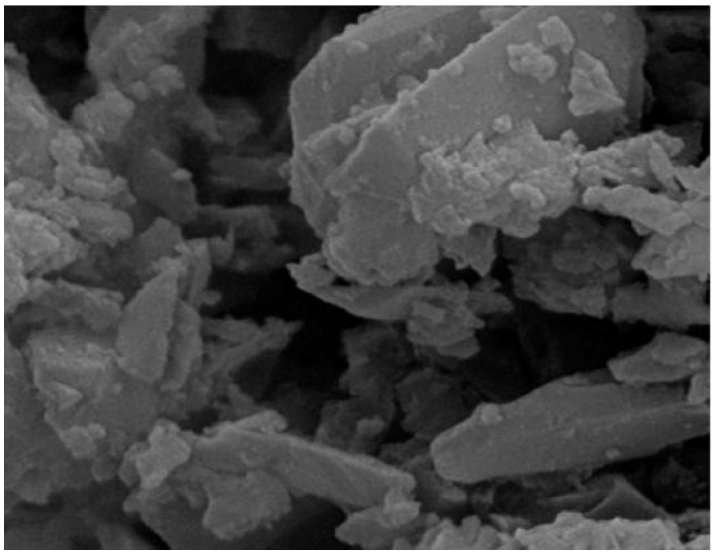

Figure 4 : SEM image of mixture of TTIP and B_4C after evaporation of isopropanol

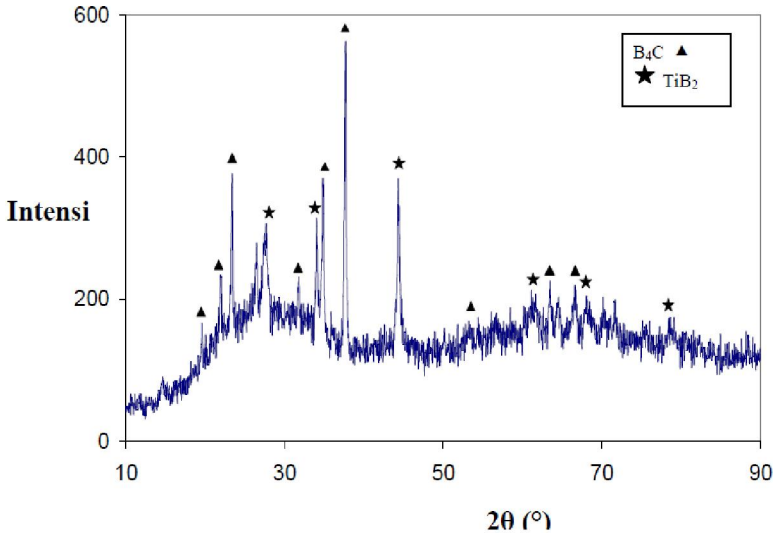

Figure 5 : XRD pattern of composies at 1523 K

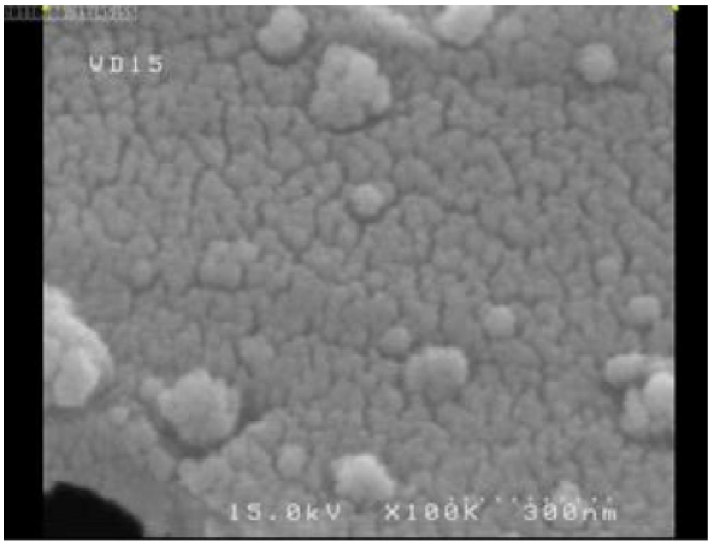

Figure 6 : SEM image of composites at 1523 K

are illustrated in Figures. 5 and 6 that were used to determine of nanoparticles size and morphologies, at 1523 K.

Also, XRD patterns and SEM images of B_4C-TiB_2 composites at 1523 K for 30 minutes with different of ww% of TiB_2 are shown in Figures 7 and 8, respectively.

RESULTS AND DISCUSSION

The JCPDS cards matching the spectra are 84-1286 for anatase TiO_2, 86-1129 for rhombohedral B_4C, 85-2083 for hexagonal TiB_2 and 73-2158 for H_3BO_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 pattern of calcination powders (TiB_2 phase in 10.0 ww%) and the fractured and ground surfaces of the B_4C-TiB_2 composites at 1523 K is shown in Figure 5. Also, Figure 6 shows SEM image of the B_4C-TiB_2 composites at 1523 K. 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 2.5 ww% in situ synthesized TiB_2 and B_4C phases were detected in composite powder at 1523 K as shown in Figure 7 (a). Most of the TiO_2 converted into TiB_2 phase at this calcination temperature. Also, it is considered that longer holding time or higher presintering temperature might be considered to decrease the amount of the remained TiO_2 at 1523 K. Figure 8 are shown SEM images of B_4C-TiB_2 composites at 1523 K for 30 minutes with 2.5, 5.0, 7.5, 10.0, 20.0 and 40.0 ww% TiB_2. Study on SEM images show that the large dark gray phases were B_4C and the small bright white nanoparticles were TiB_2 az shown in Figure 8. The results show that most size of TiB_2 nanoparticle were 10-40 nm. The TiB_2 particles dispersed in all images of the B_4C-TiB_2 specimens. The amount of in situ synthesized TiB_2 increased with increasing the $Ti(OH)_4$ content. With increasing the TiB_2 content, the grain became smaller which might improve both the flexural strength and fracture toughness of the compos-

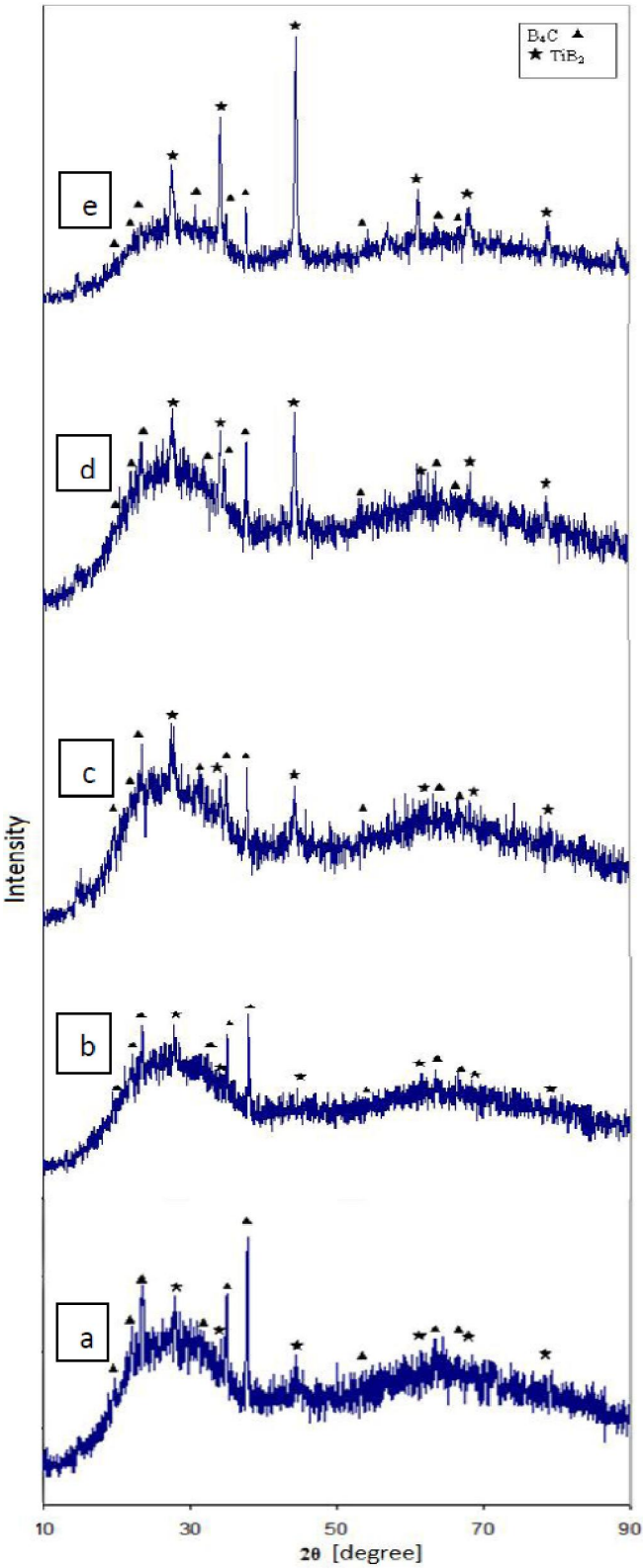

Figure 7 : XRD patterns of B_4C-TiB_2 composites at 1523 K for 30 minutes with (a) 2.5, (b) 5, (c) 7.5, (d) 20 and (e) 40 ww% TiB_2

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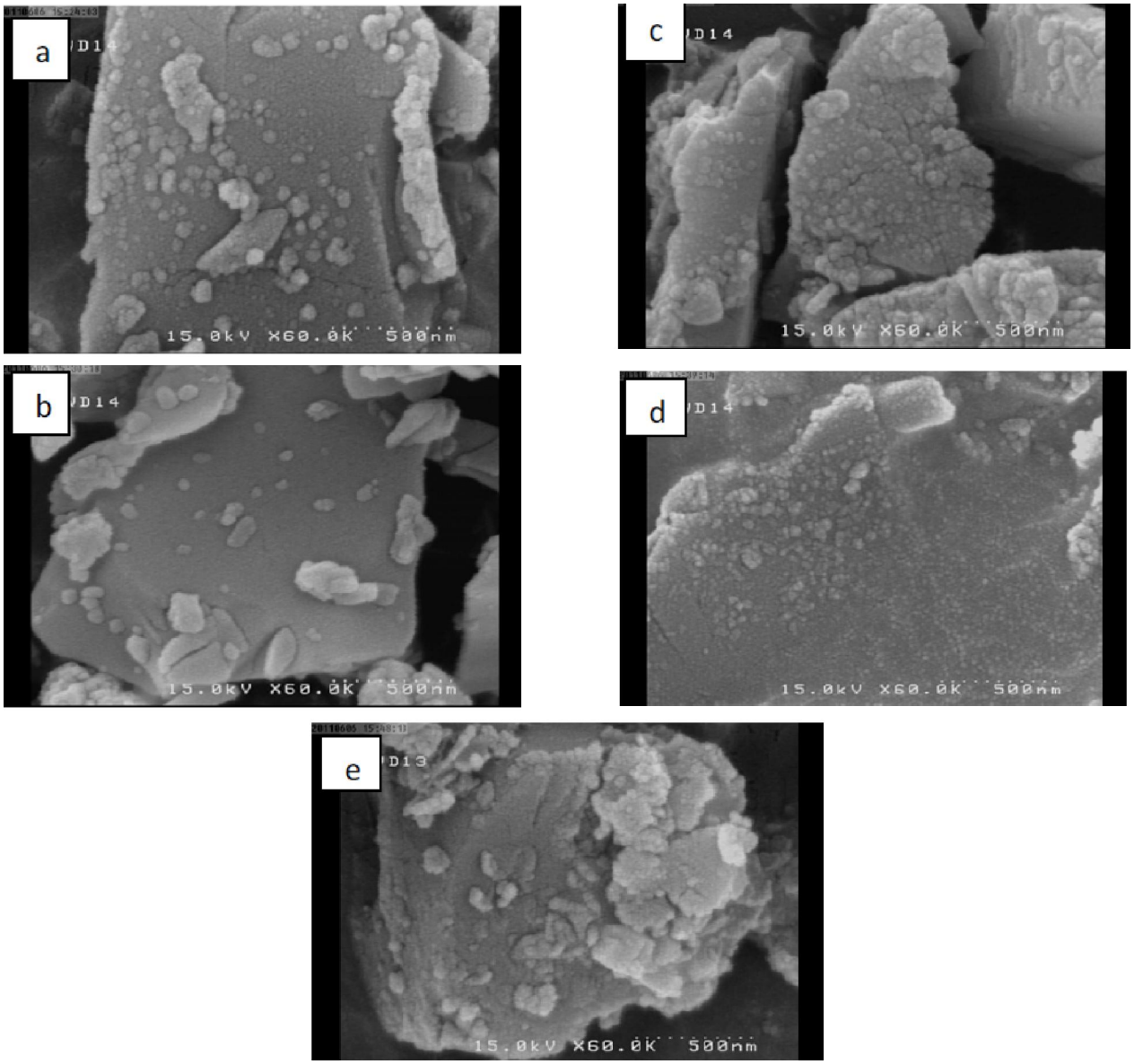

Figure 8 : SEM images of B_4C-TiB_2 composites at 1523 K for 30 minutes with (a) 2.5, (b) 5, (c) 7.5, (d) 20 and (e) 40 ww% TiB_2

ite as shown in Figure 8. XRD patterns show two phases of B_4C and TiB_2 in all ww% TiB_2 as shown in Figure 7.

CONCLUSIONS

Titanium diboride was synthesized successfully by co-precipitat method using TTIP, B_4C and isopropanol. In this research, TiB_2 in three steps produce on microstructure surfaces B_4C. In the first reaction, TTIP converted to $Ti(OH)_4$. Then TiO_2 formed from $Ti(OH)_4$ at 553 K. Finally, TiO_2 was transferred TiB_2. Calcination temperature was kept at 1523 K. The XRD and SEM results are proved which two phases of B_4C and TiB_2 at different content are identified. The nanoparticle sizes of the synthesized TiB_2 on surface of B_4C microstructures were found between 10-40 nm.

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