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A novel route to obtain B_4C nano powder via sol–gel method

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Abstract

Boron carbide nanopowders and nanowhiskers were synthesized using phenolic resin and boron alkoxide as precursors through sol–gel process in water–solvent–catalyst–dispersant system. The effects of soaking time on free carbon content and synthesized B_4C particles morphology were evaluated at 1270 °C. The synthesis process of B_4C nanopowders was completed at 1270 °C after 1 h while B_4C nanowhiskers were heterogeneously nucleated and grown from obtained nanopowders after 3 h.

Keywords: A. Sol–gel processes; Nanostructured materials; Boron carbide; Nano powder; Nano whisker

1. Introduction

Refractory carbides are experiencing an ever-growing importance and application in industry and this is mainly related to their high refractoriness and strength thereof making them suitable for cutting tools and abrasives.

Unique properties of Boron Carbide (B_4C) such as low density, high hardness and high resistance to chemical corrosion have made this non-oxide ceramic material to possess superiority over other carbides [1–6]. B_4C has wide applications in military industries like armor plates coatings, electronic industries like thermocouples and wear resistant applications like blowing nozzles [7–9]. Furthermore, boron carbide is known as one of the most important absorbent materials in nuclear industries. In fact, boron and B^{10} isotope in B_4C are extraordinary absorbents of neutron and such a tendency would end in the emission of a substantial amount of energy through Eq. (1) [10].

$$B_5^{10} + n_0^1 \rightarrow He_2^4 + Li_3^7 + 2.4\,MeV \quad (1)$$

Therefore, this material is recognized as an appropriate candidate to be employed in thermal reactors.

So far, miscellaneous techniques have been reported for the synthesis of boron carbide such as mechanical alloying and carbothermal reduction while each one suffers from particular disadvantages [11,12]. In mechanical alloying, for instance, size and morphology of particles can be hardly controlled and also, the probability of contamination with impurities is noticeable. Hence, obtaining high-purity product through this approach seems to be impossible. Nevertheless, employment of chemical routes ends in achieving a product with chemical homogeneity in molecular scale which is extremely crucial in the synthesis of high-tech ceramic bodies. Chemical methods are known as precise routes to obtain ultra-fine ceramic powders without agglomeration. Meanwhile, sol–gel method is a unique process for the synthesis of nano particles. High-purity, high chemical activity and sinterability of received product as well as possibility of mixing precursors in molecular scale are envisaged as some of the major advantages of this method [13]. Alkoxides are mostly used as precursor in sol–gel route for the synthesis of nanopowders and nanowhiskers with ideal properties such as high purity and chemical homogeneity. In this study, the efforts were mostly focused on obtaining a product with aforementioned properties as well as spherical and whisker morphology. In this respect, Soraru et al. employed boron alkoxides as boron precursor to fabricate boron-silicate glasses [14].

What should be taken into account is that the temperature has always been considered as one of the most important parameters in nano-particles synthesis process. It has been

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reported that powder particles of B_4C with uniform morphology could be synthesized through precise control of temperature. Sinha et al. have taken the advantage of boric acid as well as citric acid as the raw materials to synthesize boron carbide powder via carbothermal reduction process utilizing temperature control. The as-received product contained approximately co-axial particles with narrow sized distribution and the mean size of 2.25 μm [15]. Chen et al. synthesized boron carbide nano-particles in vacuum through reaction of boron obtained from thermal decomposition of MgB_2 with MWCNT at 1150 °C for 3 h [16]. In addition, Chang et al. heated a mixture of amorphous carbon and amorphous boron at 1550 °C in a high temperature reactor furnace to produce boron carbide nano-particles in the range of 50–350 nm and with the mean size of about 200 nm [17]. Ma et al. reported the production of boron carbide nano-wires with the mean diameter of 50 nm without utilizing catalyst and through solid–gas state mechanism occurring during reactions of carbothermal reduction process [18].

The aim of this study is to synthesize B_4C nano-particles by controlling process parameters, the most significant of which are pH, temperature as well as the time of synthesis. pH control and employment of APC in sol are helpful in controlling the particles size of precursors. Simultaneously, temperature and time seem to be effectual parameters during the synthesis process in obtaining B_4C nano-powder and nano-whisker with totally controlled morphology.

2. Experimental

Considering the sensitivity and the precision required in the synthesis of particles through sol–gel route, apposite materials were selected among the numerical available choices to obtain B_4C nano-particles.

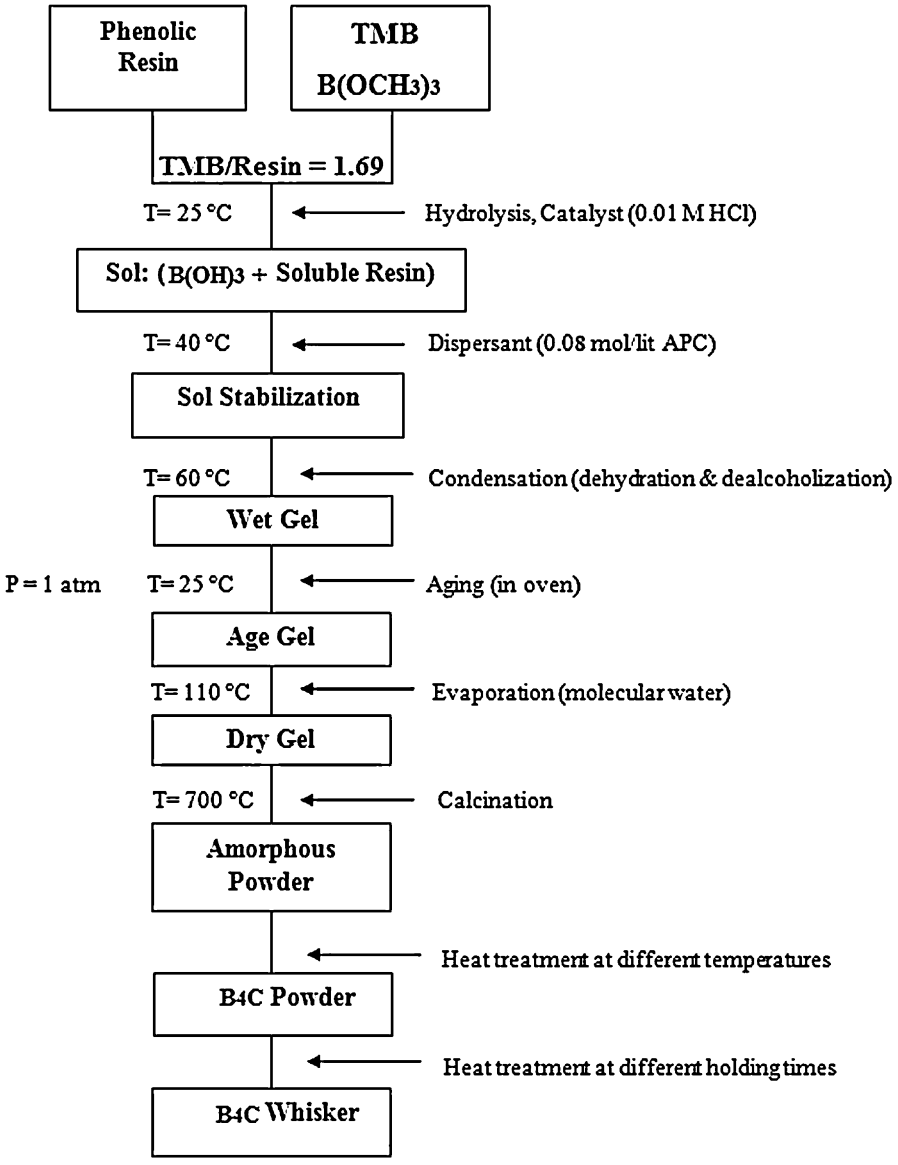

Fig. 1. Flow chart of experimental procedure.

Tetramethyl/burate (TMB, Merck Ag Germany) and Resol (RIL 800, Resitan Co., Iran) were applied, in the current investigation, as precursors for boron and carbon, respectively. In addition, HCl (Merck Ag, Germany) as catalyst, DMF (Merck Ag, Germany) as solvent, ammonium polycarboxylate (APC, D-305) as dispersant and distilled water were used in this experiment. The steps taken subsequently for the experiment are shown in Fig. 1. It is noteworthy that B_4C nano-powders and nano-whiskers were synthesized by precise control of process parameters.

Particle size analysis and stability thereof in a colloidal system were measured by DLS instrument (Malvern DTS). Furthermore, DTA/TG (STA, 404 pc) and FTIR (FTIR, SHIMADZU 8400S) were employed to investigate phase transformation in pertinent temperatures and type of bonding between the components of samples, respectively. XRD (XRD, Philips xpert) analysis was also applied to study present phases, variations in the structure of nano-particles and ultimately, calculate the rough size of crystallites. Particle size distribution was also investigated through HORIBA LB 550 instrument the process of which is based on dynamic diffraction of dispersed particles in a liquid environment. Micromeretic Gemini 2375V 4.02 was employed to specify the specific surface area of as-received particles. Moreover, precise information on size and morphology of particles and their distribution as well as the existing elements in the sample along with the crystalline structure of phases were revealed through TEM (TEM, Philips CM200) images.

In order to measure the residual carbon in the synthesized powder, a fixed amount of boron carbide powder was, initially, weighed with an accuracy of 0.0001 g (w_1) and then, heated in an electric furnace to 700 °C at 10 °C/min with a soaking time of 60 min. During this process, in addition to free carbon, some fractions of boron carbide powder are oxidized and converted to B_2O_3. The remaining powder was subsequently weighed and named w_2. The as-received powder was washed with abundant hot water passing though filter paper to remove boron oxide. During this procedure, boron carbide can hardly dissolve into hot water and hence, remains over the filter paper (w_3). The difference between w_2 and w_3 is attributed to the boron oxide removal from the powder (w_4). Therefore, the amount of oxidized boron carbide (w_5) is calculated using the weight of removed boron oxide through Eq. (2).

$$W_5 = \frac{W_4}{139.2} \times 55.2 \tag{2}$$

Conspicuously, sum of w_5 and w_3 shows the total amount of boron carbide (w_6). The difference between w_1 and w_6 could be considered as the total amount of free carbon (w_7) [12].

3. Results and discussion

Table 1 shows the variations in particle size of precursors with pH at the beginning and end of sol–gel process.

As seen, in low pH values, particularly lower than 4, particles are very fine because of low rate of hydrolysis reaction and it is related to low concentration of OH^- ions in this range of pH. Hence, the particle growth is, substantially, suppressed. Raising pH, nevertheless, leads to substantial growth of particles which could be attributed to high concentration of OH^- ions. Since precursors' particles are unstable in the sol, addition of a suitable material seems to be vital to avoid agglomeration of particles. By addition of APC (0.08 mol/l) to sol, electrostatic forces are activated which results in mean particle size of less than 10 nm and consequently, stability of precursor particles in the sol [19].

TG/DTA curves of as-synthesized powder in Argon atmosphere with the heating rate of 10 °C/min are illustrated in Fig. 2 The preliminary weight loss, as detected in TG curve, could be attributed to the loss of physical and chemical water of primary powder which is an endothermic reaction. Moreover, as exothermic reactions, decomposition and burning of organic and alcoholic compositions formed during the synthesis process could also be responsible for this phenomenon. Throughout this process in which the estimated weight loss is almost 45% all volatile compositions leave the particles. In addition, an endothermic peak is observed at around 1073 °C which could be referred to the evaporation of boron containing compositions. Fig. 3 indicating vapor pressure of boron containing compositions with oxygen confirms the results obtained through DTA experiment [20]. As seen, at around 1073 °C, the vapor pressure of B_2O_3 phase is higher than other boron containing compositions like B_2O_2 and BO and other phases are formed at higher temperatures. Nonetheless, B_2O_3 compositions in gas state react with carbon phase and convert to B_2O_2 which subsequently, results in formation of B_4C nuclei according to Eq. (3). Following this substantial endothermic reaction, $B_2O_{2(g)}$ reacts with carbon solid particles through solid–gas mechanism at around 1270 °C and form B_4C nano-particles via the final endothermic reaction according to Eq. (4).

$$B_2O_{3(l)} + C_{(s)} \rightarrow B_2O_{2(g)} + CO_{(g)} \tag{3}$$

$$2B_2O_{2(g)} + 5C_{(s)} \rightarrow B_4C_{(s)} + 4CO_{(g)} \tag{4}$$

X-ray diffraction patterns of synthesized powder at 1270 °C with the soaking times of 1, 2 and 3 h are shown in Fig. 4. It could be seen that by augmenting the soaking time, the intensity of peaks, attributed to rhombohedral crystal system of B_4C, has been observed to increase. Therefore, it could be concluded that augmenting the soaking time lets the materials involved in the reaction of B_4C synthesis have sufficient time for chemical reaction. In fact, during this phenomenon, more CO and B_2O_2

Table 1
The effect of pH on particle size.

pH	Particle size (nm)	
	Before aging	After aging
4	2.6	1.6
4.5	2.8	2.6
5	3.1	3.5
5.5	3.8	5.9
6	6.8	8.9
6.5	10.9	12
6.9	18.0	16.1

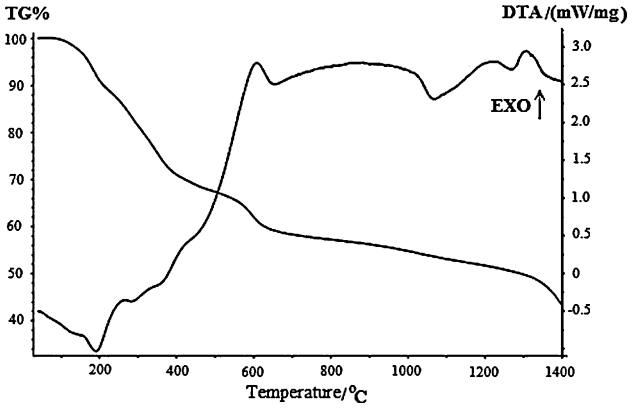

Fig. 2. Thermal behavior for synthesized gel powder heated from 25 to 1400 °C with heating rate of 10 °C/min.

gas phases are formed and hence, the system would change gradually from solid to gas state which could ameliorate the synthesis circumstances significantly. These factors would totally end to reduction of carbon impurity in the final obtained powder. The presence of carbon in the product is an indication of incomplete reaction of precursors in the system and also, waste of some amount of boron during carbothermal reduction. Calculations show that the amount of residual carbon at 1270 °C with the soaking time of 1 h is 8.75% which decreases to 6.25% when the synthesis time increases to 3 h. It means that solid carbon and gas phases' derivatives thereof including CO and CO_2 are consumed for the formation of B_4C or removed from the system with time.

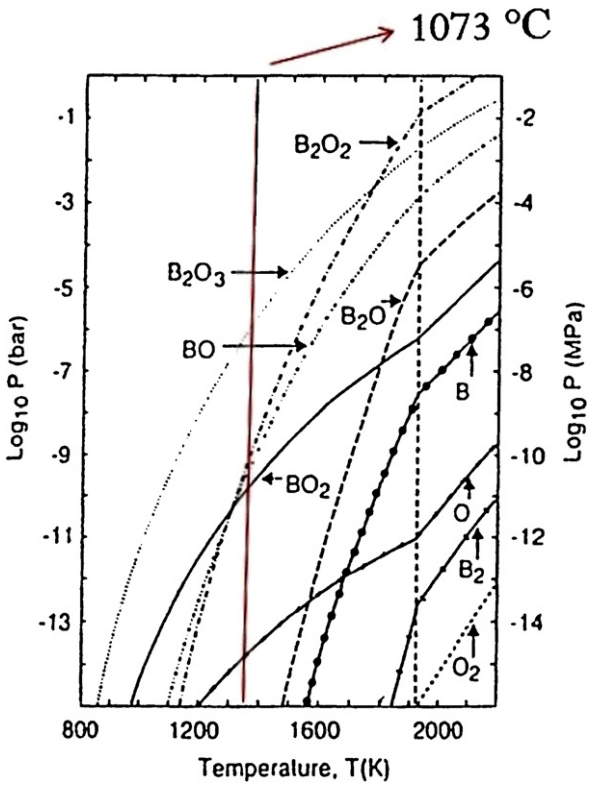

Fig. 3. Vapor pressure of B–O compound at different temperature [20].

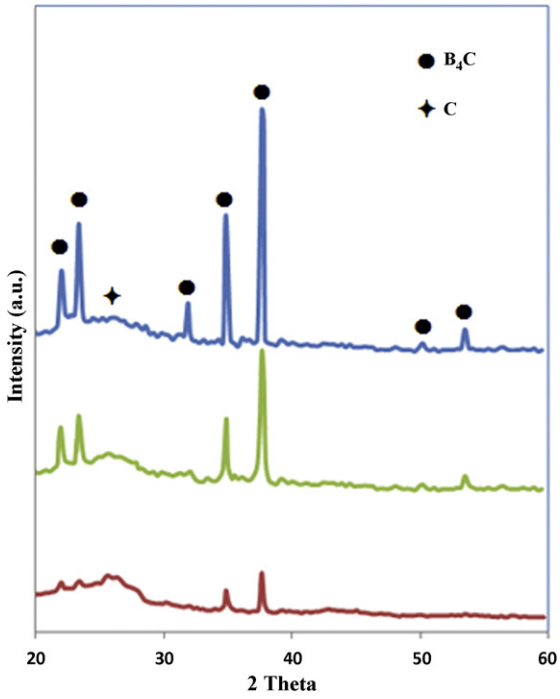

Fig. 4. X-ray diffraction pattern for powder synthesized at 1270 °C for holding times of 1 h, 2 h and 3 h.

Numerical calculations illustrate that B_4C crystallite size, which is synthesized at 1270 °C, for 1 h, is about 12.2 nm. By increasing the synthesis time up to 3 h it increases to 17.6 nm. Such variation in size confirms the significant role of time for atomic diffusion in the arrangement of lattice units and subsequently, enlargement of crystallites. Therefore, escalation of the synthesis time at a constant temperature causes the growth of formed crystallites along the preferred orientations. Fig. 5 illustrates the FTIR analysis of B_4C powder synthesized at 1270 °C with the soaking time of 2 h. As indicated, a strong peak is observed at around 1190 cm^{-1} which is related to B–C bonds [21]. In addition, there is a fairly strong peak at about

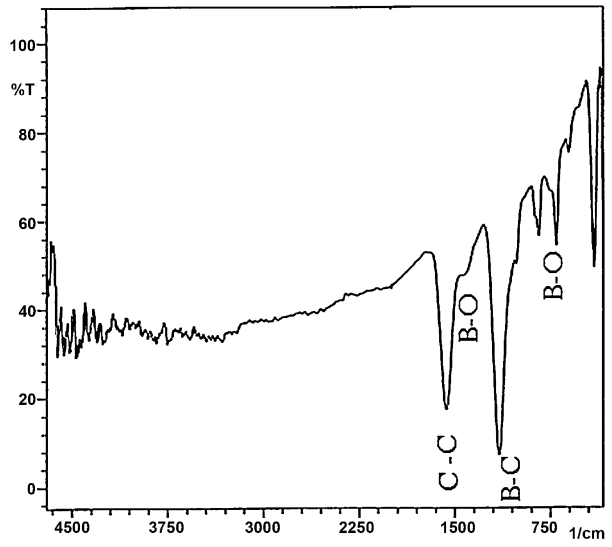

Fig. 5. FTIR analysis of B_4C powder.

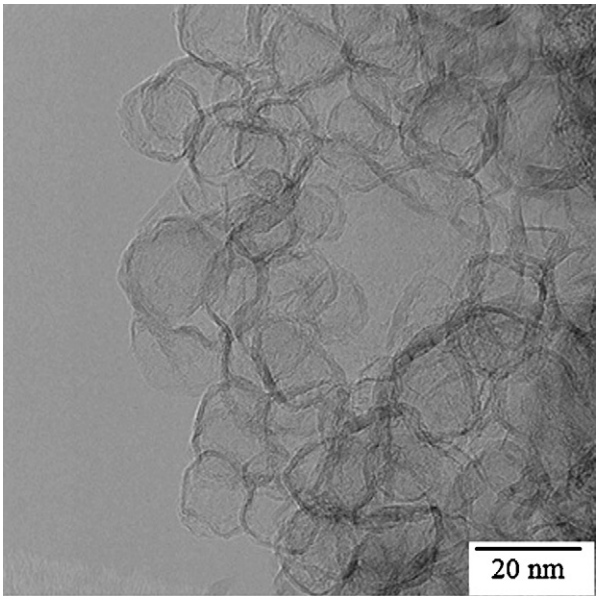

Fig. 6. TEM image of synthesized powder at 1270 °C for 1 h.

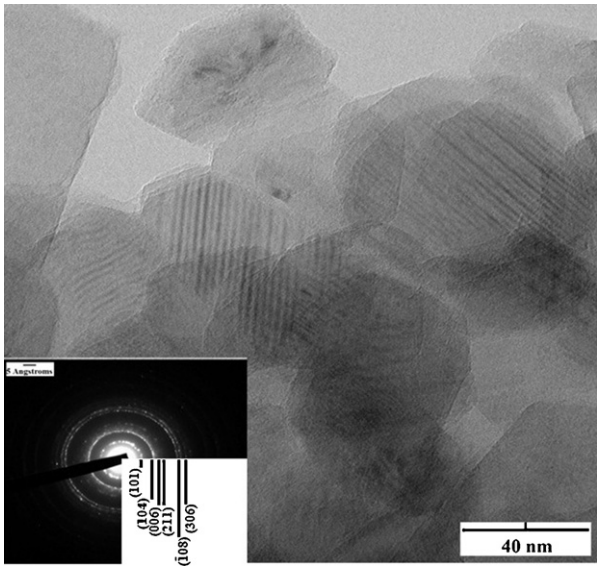

Fig. 8. TEM image along with diffraction pattern of synthesized powder at 1270 °C with the soaking time of 2 h.

1570 cm^{-1} which could probably be attributed to C–C bonds. B–O bonds could also be detected through the peaks appeared at 1450 and 750 cm^{-1}.

TEM image along with the diffraction pattern of synthesized powder at 1270 °C with the soaking time of 1 h is shown in Fig. 6. It could be observed that synthesized B_4C particles have mono-size distribution with similar cross section displaying spherical morphology. Furthermore, it seems that B_4C particles have mean particle size of 10–30 nm. The diffraction pattern of these particles illustrated in Fig. 7 consists of several rings indicating that B_4C nano-particles have converted from amorphous to crystalline phase gradually.

Fig. 8 displays TEM image along with diffraction pattern of synthesized powder at 1270 °C with the soaking time of 2 h. In accordance with this image, the mean particle size varies from 20 to 40 nm and the morphology of particles seems to follow a uniform pattern. Moreover, the diffraction pattern of these particles reveals that synthesized B_4C particles are very fine and fully crystalline.

TEM image and diffraction pattern of synthesized powder at 1270 °C with the soaking time of 3 h is illustrated in Fig. 9. It could be seen that B_4C whiskers have mostly nucleated from carbon and B_4C nano-particle surfaces and are growing along preferred orientations heterogeneously. In addition, nano-powders and nano-whiskers could be observed simultaneously in this stage of synthesis process. It is noteworthy that synthesized nano-whiskers have the mean diameter of 20–40 nm. Fig. 10 shows HRTEM images of synthesized powder

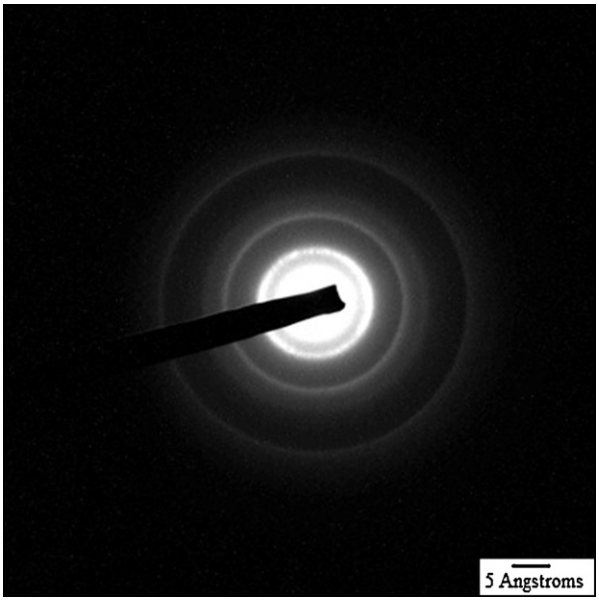

Fig. 7. Diffraction pattern of synthesized powder at 1270 °C for 1 h.

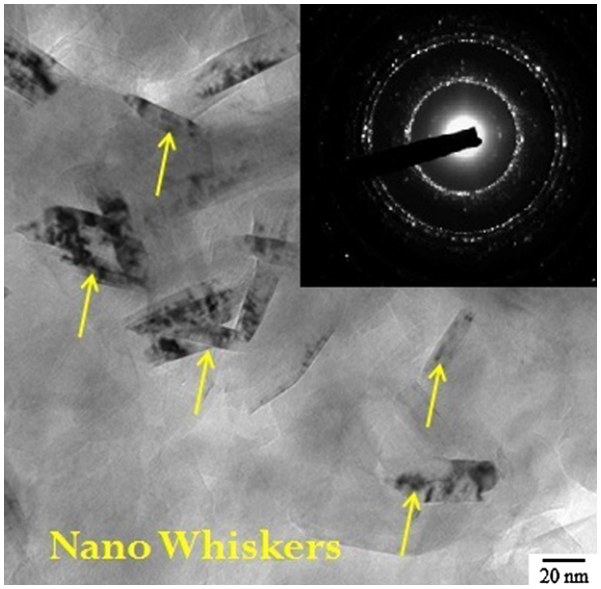

Fig. 9. TEM image and diffraction pattern of synthesized powder at 1270 °C with the soaking time of 3 h.

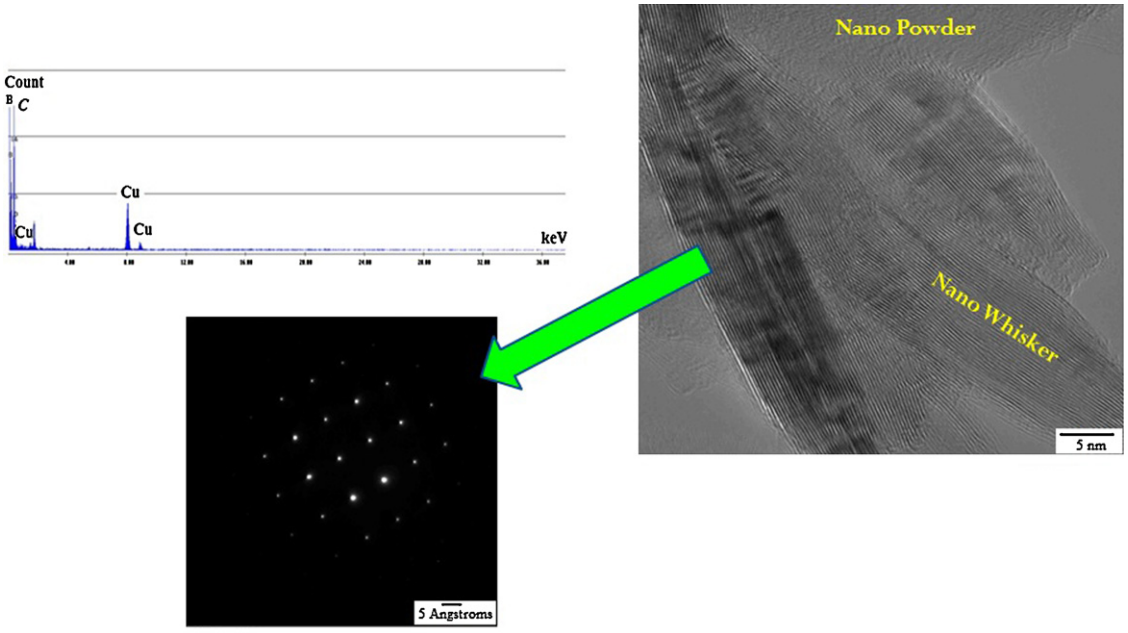

Fig. 10. HRTEM images of synthesized powder together with diffraction pattern and EDS analysis at 1270 °C with the soaking time of 3 h.

together with diffraction pattern and EDS analysis thereof. This figure indicates that B_4C nano-whiskers have grown from the surface of particles along the preferred orientation of [0 1 2] through solid–gas mechanism. Furthermore, the diffraction pattern proves that single crystal nano-whiskers are formed during the synthesis process and atomic planes thereof are arranged orderly. EDS analysis from B_4C whiskers shows the presence of B and C elements.

4. Summary

In this study, the effect of significant parameters such as pH, temperature and time on the synthesis of B_4C nano particles was investigated. The obtained results showed that by controlling pH and addition of APC as dispersant into the sol, precursors' particles could be maintained lower than 10 nm. DTA analysis revealed that the nucleation of B_4C particles commences at about 1270 °C. XRD patterns confirmed the presence of B_4C phase in disparate diffraction planes. In addition, the crystallite sizes of synthesized powder indicated that by controlling time and temperature, ultra-fine crystallites (smaller than 15 nm) could be synthesized accordingly. B–C bonds could also be observed through FTIR studies of the final product which was mainly related to formation of B_4C. Moreover, TEM and HRTEM instruments revealed the morphology of nano-powder and nano-whisker structures. TEM images of synthesized B_4C nano-powder showed that the mean particle size of nano-powders with spherical morphology was between 10 and 30 nm. Also, it was displayed that as-received nano-powders have a poly-crystalline structure which converts totally to crystalline after the soaking time of 2 h while the particle size was maintained less than 40 nm. Furthermore, B_4C nano-whiskers nucleated from powder particles heterogeneously and grew along the preferred orientation of [0 1 2]. The prior studies show that B_4C nano-powders mostly form through solid–gas reactions ($B_2O_{2(g)}$–$C_{(s)}$) while formation of nano-whiskers succeeds gas–gas reactions ($B_2O_{2(g)}$–$CO_{(g)}$).

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