Synthesis of B$_4$C - Nano TiB$_2$ Composite Nano Powder by the Chemical Precipitation Method

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Abstract: The aim of this research is to determine the proper concentration of Titanium Tetra IsoPropoxide (TTIP) and select the right temperature and time of calcinations for the synthesis of B$_4$C-nano TiB$_2$ composite Nano powder by the chemical precipitation method. For this purpose, first, solutions with TTIP molar concentrations of 0.1, 0.05 and 0.03 were prepared and the optimal molar concentration of TTIP was determined to be 0.05. Then, a diluted solution of distilled water and TTIP was mixed with Isopropanol Alcohol containing B$_4$C micropowder. In this mixture, Titanium Hydroxide nanoparticles were initially synthesized and then, to convert the Ti(OH)$_4$ to TiB$_2$, the above mixture were calcined in a furnace, under Argon atmosphere. The calcination process was carried out at temperatures of 750, 1000 and 1250 ℃. It was observed that the most suitable temperature for the formation of the TiB$_2$ phase is 1250 ℃ and that the lower temperatures only lead to the formation of the TiO$_2$ phase. It was also observed that, at the calcination temperature of 1250 ℃, the most appropriate time duration for the conversion of Ti(OH)$_4$ nanoparticles to TiB$_2$ nanoparticles is 30 minutes, during which B$_4$C-nano TiB$_2$ composite Nano powders form, with most of the TiB$_2$ particle sizes being in the range of 30-60 nm.

Keywords: B$_4$C-nano TiB$_2$, Chemical precipitation, Nano powder, TTIP

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1   INTRODUCTION

Boron carbide, with a density of 2.4-2.52 g/cm^3, melting point of 2447 °C and a boiling temperature higher than 3500 °C, is the hardest material after diamond and cubic Boron Nitride. Because of these properties, boron carbide is used in many industrial and strategic applications[1], [2]. However, due to the existence of covalent bonds between carbon and boron, low plasticity, high resistance against grain boundary slippage, and low surface stress in a solid state, boron carbide has a relatively low sintering ability and fracture toughness.

The strong covalent bond results in a low self-diffusion; this prevents compaction by the solid state sintering methods or requires very high sintering temperatures [3], [4]. On the other hand, the homogeneous mixing of the primary ceramic powder and sintering aids is difficult and it needs special equipment such as a grinding mill and also prolonged operations, which not only take time and lead to not-so-homogeneous mixing but also may bring some impurities into the powder mixtures.

The use of Titanium diboride in powder, oxide or carbide forms, as an effective sintering aid, has been investigated by many researchers [5]. The higher mechanical properties of TiB$_2$ can improve the fracture toughness and the bending strength of boron carbide. Moreover, since no chemical reaction occurs between these two materials, it is possible to make a composite out of these materials. The electrical conduction is expected to vary from metallic behavior of TiB$_2$ to semiconducting behavior of B$_4$C [6].

B$_4$C-TiB$_2$ ceramic composites with a certain amounts of TiB$_2$ led to high electrical conductivity that could satisfy the demand of electrical discharge machining (EDM) and making the machining of B$_4$C-TiB$_2$ composites easy and cheap [7-8]. A fine-grained composite powder with a homogeneous distribution of TiB$_2$ and B$_4$C is required to prepare dense and tough sintered compacts in this system [9].

As was mentioned, one of the most crucial problems of adding the TiB$_2$ powder to B$_4$C powder is its non-uniform distribution in the structure of the final powder. This problem is expected to be remedied to some extent by the synthesis of TiB$_2$ nanoparticles among the particles of the B$_4$C powder. So, in this research, the optimum concentration of TTIP was first determined and then the effects of the temperature and time of calcination on the phase composition and morphology of B$_4$C-nano TiB$_2$ composite nano powder obtained by chemical precipitation were investigated.

2   MATERIALS AND METHODS

The constituent materials for the synthesis of the B$_4$C-nano TiB$_2$ composite nano powder include boron carbide with a molecular weight of 55 g/mol, Titanium Tetra IsoPropoxide (TTIP) solution (Ti[OCH(CH$_3$)$_2$]$_4$) with a molecular weight of 284 g/mol and 97% purity, Ethanol, Isopropanol alcohol (C$_3$H$_7$OH) with 99.6% purity and distilled water. To obtain the proper concentration of TTIP for the synthesis of the B$_4$C-nano TiB$_2$ composite nano powder, 0.03, 0.05 and 0.1 molar concentrations of this material were analyzed and then, considering the percentage of TiB$_2$ (10%), the volume of the alcohol solvent was used and the optimum amount of TTIP were determined.

Since the source of Titanium is TTIP, which is quickly hydrolysed in reaction with water, the use of a suitable solvent which is compatible with the type of process and primary materials plays a significant role in achieving the desired product; so in this research, Ethanol and Isopropyl alcohol were chosen for investigation. Then, compounds with 10 g of B$_4$C powder, 4.4 g of TTIP liquid, 310 ml of Isopropanol alcohol and 3 ml of distilled water were prepared.

Flow chart for synthesis of B$_4$C-nano TiB$_2$ composite Nano powder is shown in Fig. 1. As it can be seen, first, two beakers, with each one containing 5 g of boron carbide powder and 155 ml of alcohol, were prepared and mixed separately by magnetic mixers to yield two solutions with equal concentrations of B$_4$C. During mixing, 4.4 g of TTIP was added to one of the beakers and 3 ml of distilled water was added to the other beaker. The diluted solution of distilled water and alcohol was gradually added to the TTIP solution in order to prevent its quick hydrolysis and to stop the formation of coarse particles of Titanium Hydroxide.
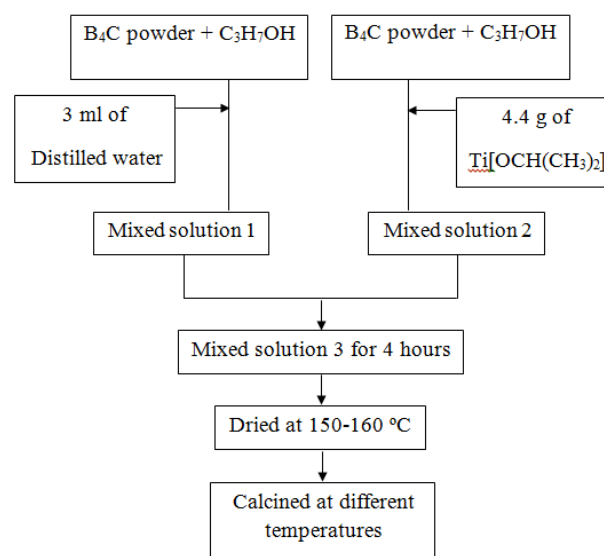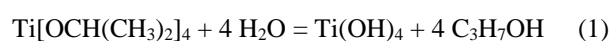

Fig. 1   Flowchart for synthesis of B$_4$C-nano TiB$_2$ composite Nano powder

The solution obtained by mixing the distilled water with TTIP diluted in alcohol that contained the primary boron carbide powder was mixed for 4 hours by a magnetic mixer in order for the Titanium Hydroxide particles to form on the boron carbide particles. Then, the resulting solution was placed inside an oven at a temperature of about 150-160 ℃ in order to evaporate the alcohol and get the B_4C powder with the $Ti(OH)_4$ particles. A sample of the above powder was subjected to thermal analysis test (DTA/TG) in order to determine the optimal calcination temperature for the conversion of $Ti(OH)_4$ to TiB_2. Other samples were subsequently placed in the furnace under Argon atmosphere, in graphite crucibles, and heated to 750, 1000 and 1250 ℃ for 30 and 60 minutes, at a heating rate of 10 ℃/min. To study the phase changes in these samples, their XRD spectra were prepared and then SEM images were acquired to evaluate the size and morphology of particles.

3 RESULTS AND DISCUSSION

Firstly, to find the right solvent, Ethanol and Isopropyl alcohol were evaluated. The tests performed with Ethanol indicated the early hydrolysis of TTIP before it is added to the system. Even when Ethanol of high purity was used, it was observed that TTIP gradually hydrolyzes and white flocks of Titanium Hydroxide start to form and precipitate in the system. So, it was concluded that even pure Ethanol contains water molecules in its structure that hydrolyze the TTIP. By using Isopropyl alcohol instead of ethanol, no change was observed in the system and even as time passed, there was no sign of Isopropyl alcohol reacting with TTIP and forming the Titanium Hydroxide flocks. Thus, Isopropyl alcohol is a suitable solvent and compatible with the process and primary materials used in this research.

Then to determine the proper concentration of TTIP for the synthesis of the B_4C-nano TiB_2 composite Nano powder, 0.1, 0.05 and 0.03 molar concentrations of TTIP were analyzed. When using the TTIP as a primary material, due to its reaction with water and the hydrolysis of TTIP, solid particles of Titanium Hydroxide ($Ti(OH)_4$) form according to reaction (1).

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

When a solution contains a specific concentration of TTIP, during the hydrolysis, the amount of $Ti(OH)_4$ gradually increases with time. As the solution reaches its lowest concentration for nucleation, a nucleus forms and starts to grow. This reduces the concentration of the solution. When the solution reaches a concentration lower than the lower bound needed for nucleation, a

considerable growth takes place. This nucleation can have a homogeneous or inhomogeneous form or be a combination of the two. Since from the standpoint of the needed formation energy, inhomogeneous nucleation is more likely to form, and it occurs at lower activation energy, it takes place at lower concentrations relative to the homogeneous nucleation process [10]. B_4C particles in the solution can be considered as appropriate places for the nucleation and growth of $Ti(OH)_4$ particles.

In view of this fact, if the solution's concentration is greater than the minimum concentration needed for homogeneous nucleation, the $Ti(OH)_4$ phase will form away from the surfaces of B_4C particles and between these particles; therefore, a mix of $Ti(OH)_4$ and B_4C particles will be obtained. However, if the concentration of the solution is less than the minimum concentration needed for homogeneous nucleation, the $Ti(OH)_4$ phase will form inhomogeneously on the surfaces of B_4C particles.

Figs. 2, 3 and 4 illustrate samples with 0.1, 0.05 and 0.03 molar TTIP concentrations, respectively. As it is shown in Fig. 2, a large number of spherical particles of $Ti(OH)_4$ phase have formed between the B_4C particles. The average size of the $Ti(OH)_4$ particles is 400 nm. Therefore, the molar concentration of 0.1 is greater than the minimum concentration necessary for homogeneous nucleation and the $Ti(OH)_4$ phase has formed away from the surfaces of B_4C particles and between them; and what is observed is a mix of B_4C and $Ti(OH)_4$ particles.
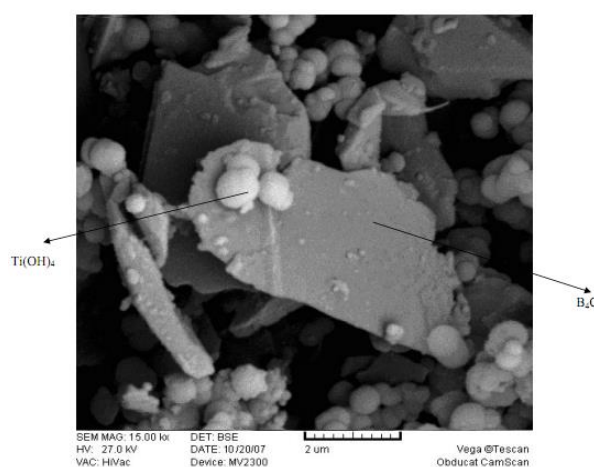

Fig. 2   The SEM image of the sample with 0.1 molar concentration of TTIP, the spherical particles of $Ti(OH)_4$ have formed between the B_4C particles

Fig. 3 shows the image of the sample in which the molar concentration of TTIP has been reduced to 0.05. This figure clearly shows that the spherical particles of $Ti(OH)_4$ are on the surfaces of B_4C particles and the average size of $Ti(OH)_4$ particles is less than 100 nm.

Considering the fact that inhomogeneous nucleation occurs at lower concentrations compared to homogeneous nucleation, it seems that the concentration of solution in this sample is in the range of inhomogeneous nucleation and that the B_4C particles in the solution have acted as suitable places for the nucleation and growth of $Ti(OH)_4$ particles.
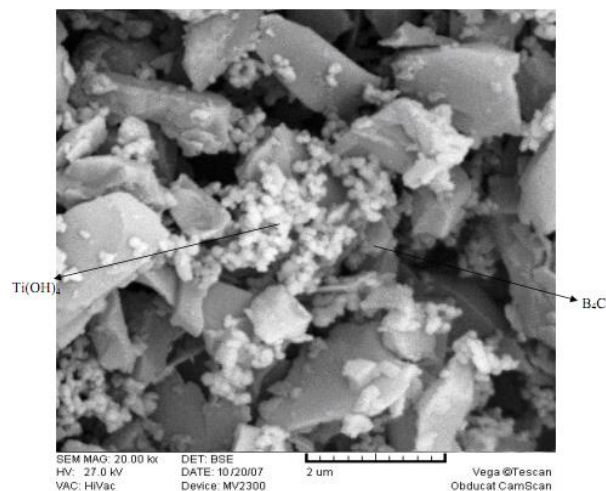

Fig. 3   The SEM image of the sample with 0.05 molar concentration of TTIP; the spherical particles of $Ti(OH)_4$ formed on the B_4C particles
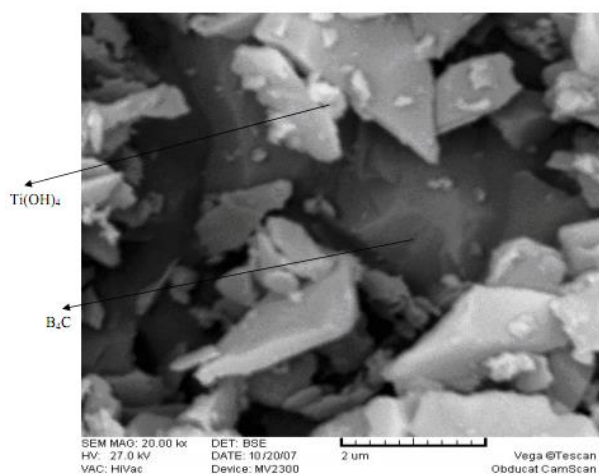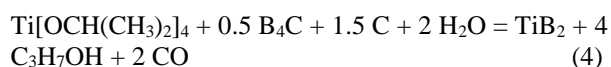

Fig. 4   The SEM image of the sample with 0.03 molar concentration of TTIP, a small fraction of B_4C particles has been covered with $Ti(OH)_4$ particles

As is observed in Fig. 4, with the reduction of the solution's molar concentration to 0.03, a small fraction of $Ti(OH)_4$ spherical particles have formed on the surfaces of and between the B_4C particles. Thus, the TTIP molar concentration of 0.05 has been considered as appropriate, and all the investigations in this paper have been carried out at this concentration.

In the general process of synthesizing the B_4C-nano TiB_2 composite Nano powder by the chemical precipitation method, by mixing the TTIP and distilled water diluted with alcohol in an alcohol medium containing the primary boron carbide powder, first, reaction (1) takes place and titanium hydroxide nanoparticles form on the surfaces of boron carbide particles. Then, after the calcination of this powder in an oven, reactions (2) and (3) take place successively, resulting in the formation of TiB_2 nanoparticles on the particles of B_4C powder. The sum of reactions (1), (2) and (3) is written as general reaction (4). It's been reported in the literature that the $Ti(OH)_4$ phase is very unstable, and that with the rise of temperature in the range of 250-300 ℃, it is transformed to the stable TiO_2 phase, according to reaction (2) [5].

$$Ti(OH)_4 = TiO_2 + 2\ H_2O \qquad (2)$$

$$TiO_2 + 0.5\ B_4C + 1.5\ C = TiB_2 + 2\ CO \qquad (3)$$

$$Ti[OCH(CH_3)_2]_4 + 0.5\ B_4C + 1.5\ C + 2\ H_2O = TiB_2 + 4\ C_3H_7OH + 2\ CO \qquad (4)$$

It has also been reported that the conversion of the TiO_2 phase to TiB_2 in the presence of B_4C, according to reaction (3), requires temperatures higher than 1080 ℃ [8], [11]. In this research, the thermal analysis test of DTA-TG was performed in a neutral gas (Argon) atmosphere in order to achieve, with a high approximation, the temperature range for the above-mentioned reactions. The results of the thermal analysis test performed on a powder sample containing TiB_2 with 10% weight have been presented in Fig. 5 as DTA and TG curves.
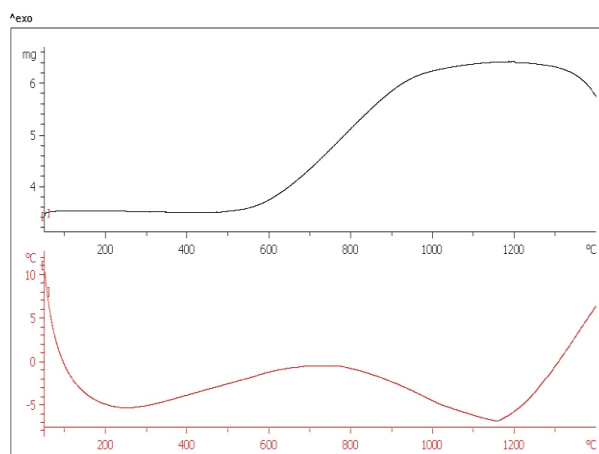

Fig. 5   Curves of DTA and TG thermal analyses performed on the nanocomposite powder sample

In view of the results of the DTA-TG thermal analysis test, it is observed that an endothermic reaction has occurred at a temperature of about 280 ℃, resulting in

a considerable weight loss. This reaction is the same as reaction (2), which results in the loss and evaporation of water from the $Ti(OH)_4$ phase and the formation of the TiO_2 phase.

Another extremely endothermic reaction (reaction (3)) occurs at a temperature of about 1250 ℃ and leads to the formation of TiB_2 Nano powders. These results indicate that, under the current laboratory conditions, the synthesis of the B_4C-nano TiB_2 composite Nano powder by calcinating the B_4C powder mixture that contains the $Ti(OH)_4$ phase is possible at temperatures higher than 1250 ℃, and that the calcination operation at lower temperatures will only lead to the synthesis of TiO_2 containing B_4C powder.

The reasons that the temperature of reaction (3), obtained from the DTA-TG thermal analysis test, is higher than the thermodynamic temperature of the above reaction are the non-standard conditions of the test and also the high rate of heating (10 ℃/min). Most probably, this causes the temperatures of the sample's internal regions to reach the oven temperature at a later time and the above reaction to take place at a higher apparent temperature.
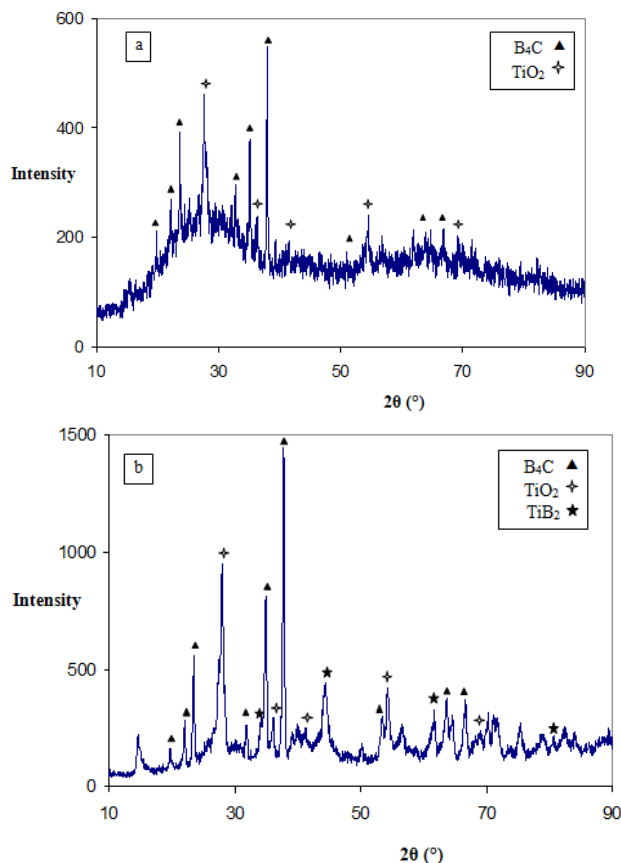
To make sure that the temperature of reaction (3), under the experimental conditions of this research (10 ℃/min), is the same temperature (1250 ℃) obtained from the DTA-TG thermal analysis test, samples of the composite powder were calcinated at temperatures of 750, 1000 and 1250 ℃ for 30 and 60 minutes and then their XRD spectra and SEM images were prepared. The calcination of the B_4C powder containing the $Ti(OH)_4$ nanoparticles at 750 ℃ for 60 min and the analysis of its XRD diagram (shown in Fig. 6(a)) indicate that the above sample only contains the B_4C and TiO_2 phases. This demonstrates that by raising the temperature to about 280 ℃, reaction (2) has occurred, while by further increasing the temperature to 750 ℃, reaction (3) has not occurred and the TiB_2 phase has not formed.

According to Fig. 6(b), the XRD spectrum obtained from the sample that was calcinated at 1000 ℃ for 60 min shows that small amounts of the TiB_2 phase have formed in this sample, in addition to the B_4C and TiO_2 phases, which indicates the slight progress of reaction (3). This may be caused by a lack of precision tuning of the oven temperature and not keeping the interior temperature constant; in other words, having a temperature tolerance. Most probably, this temperature tolerance may have sometimes brought the oven temperature to about 1080-1100 ℃ in the regions close to oven elements. As a result, the necessary thermodynamic conditions for the implementation of reaction (3) have been partially provided at those points and minor amounts of the TiB_2 phase have formed.
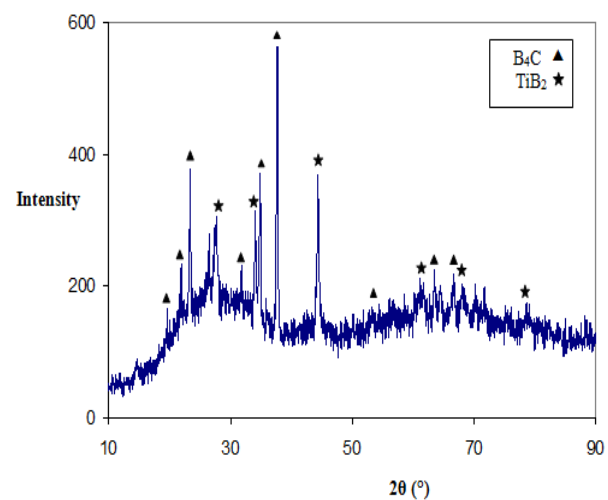

Fig. 6   Phase analysis of the nanocomposite powder after its calcination in an oven under Argon atmosphere for 60 min and at temperatures of (a) 750 ℃ and (b) 1000 ℃

Fig. 7   The XRD diagram of the nanocomposite powder after its calcination in an oven under Argon atmosphere for 30 min and at a temperature of 1250 ℃

Fig. 7 shows the XRD spectrum of a sample after its calcination at a raised temperature of 1250 ℃ and a reduced operation time of 30 min (to prevent the

growth of Nano-size particles). It is observed that the above sample only contains the B_4C and TiB_2 phases. This means that, with a gradual increase of oven temperature to 280 ℃, first, the $Ti(OH)_4$ phase has been converted to TiO_2, according to reaction (2), and then at temperatures between 1000-1250℃ (probably close to 1250 ℃), the TiO_2 phase has been completely converted to TiB_2, according to reaction (3).
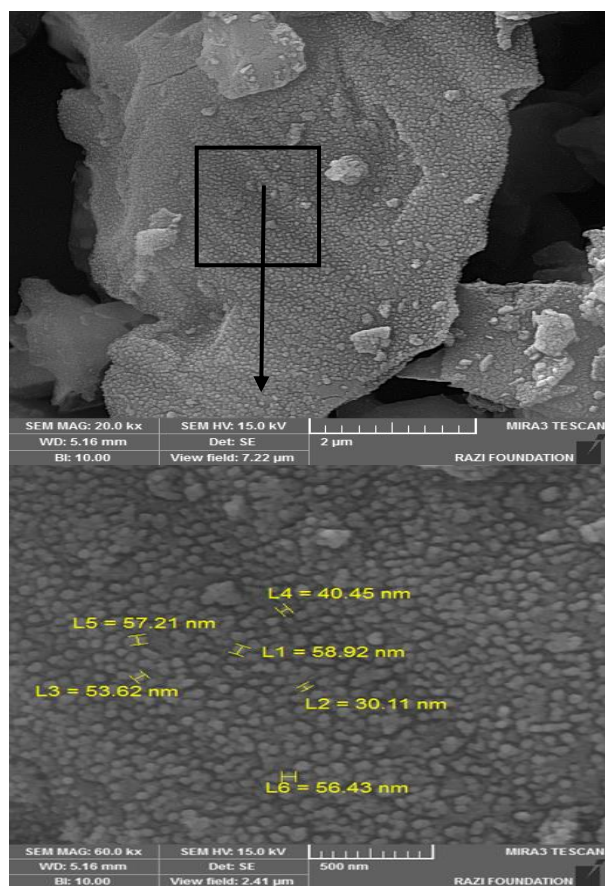

Fig. 8   FE-SEM images taken from the nanocomposite powder after its calcination in an oven under Argon atmosphere for 30 min and at a temperature of 1250 ℃

In order to study the morphology and size of TiB_2 particles formed on the boron carbide particles, FE-SEM images were acquired of the composite powder after calcination at 1250 ℃ for 30 min (see Fig. 8). These images show that the formed TiB_2 phase is totally Nano in dimension, and that its particles are smaller than the primary $Ti(OH)_4$ particles and the produced TiO_2 particles. Most of the particles in this phase consist of nanoparticles with sizes of 10-40 nm that have formed on the micron-size particles of boron carbide. The reason for the reduction of average particle size is the selection of proper temperature and time for the operation, which has caused the nucleation and growth of Nano-size TiB_2 particles within a short time (according to reaction (3)), and this short period of time has prevented the excessive growth of particle sizes. Based on the XRD results presented in Figs. 6 and 7 and the SEM images in Fig. 8, it is observed that the temperature of 1250 ℃ and time of 30 min provide the best conditions for the conversion of Nano-size $Ti(OH)_4$ to Nano TiB_2 and the formation of B_4C-nano TiB_2 composite Nano powder. The appropriateness of temperature 1250 ℃ had already been verified by the results of DTA-TG thermal analysis test (Fig. 5).

4   CONCLUSION

If the TTIP solutions' molar concentration is 0.05, the solution will be in the inhomogeneous nucleation range and the B_4C particles in the solution will act as suitable places for the nucleation and growth of $Ti(OH)_4$ particles. After calcination at temperatures of 750, 1000 and 1250 ℃, it was observed that the 1250 ℃ is the most suitable temperature for the formation of the TiB_2 phase and that the lower temperatures only lead to the formation of the TiO_2 phase. It was also found that, at the calcination temperature of 1250 ℃, a 30 min duration is quite appropriate for the conversion of $Ti(OH)_4$ nanoparticles to TiB_2 nanoparticles and that this calcination period leads to the formation of B_4C-Nano TiB_2 composite Nano powders in which most of the TiB_2 particles have sizes in the range of 30-60 nm.

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