



Obtaining ultrafine powders of some boron carbide-based nanocomposites using liquid precursors**

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Due to their unique set of physical and chemical properties, boron carbide-based composites have become the hard materials most widely used in current high technologies. However, the range of possible applications of these materials is narrowed because of boron carbide's brittleness and low resistance to cracking. This problem can be resolved by creating nanocrystalline structures from sufficiently finely dispersed starting materials. Several novel technological routes of direct chemical synthesis of finely dispersed boron carbide/metal diboride composite powders from liquid precursors are elaborated.

Keywords: boron carbide-based composite, chemical synthesis, liquid charge

1. Introduction

Among the hard materials widely used in current high technologies, boron carbide (with approximate chemical formula B_4C) has the highest hardness-to-density ratio. This and a number of other unique physical and chemical properties make boron carbide-based hard

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materials attractive for a variety of industrial applications.¹ But, the range of possible applications of these materials is narrowed due to boron carbide's brittleness and, consequently, relatively low resistance to cracking.

In principle, this problem can be resolved by creating nanocrystalline structures of boron carbide-based heteromolecular composite materials. But, it is possible only if the starting materials are sufficiently finely dispersed. From a number of existing boron carbide-based multicomponent systems, boron carbide alloys with metal M diborides B_4C-MB_2 seem to be the most promising in this regard. Their chemical synthesis from liquid precursors can be conducted at relatively moderate temperatures and provides high purity product in finely powdered form.

In this paper, first the recent technologies of obtaining B_4C and MB_2 fine powers from liquid charges are concisely summarized. The key conclusion is that these processes are quite similar and joint chemical treatment of their precursors should directly lead to syntheses of finely dispersed composite powders useful for further consolidation to form hard nanocomposite materials. Inspired by this perspective, here we propose several original technologies of direct synthesis of finely dispersed B_4C-MB_2 composite powders from corresponding liquid precursor materials.

2. Synthesis of powder components of B_4C-MB_2 composites

2.1 Synthesis of B_4C powders

Polymers are frequently used to obtain powders of inorganic materials. In particular, boron carbide precursor ceramic powders are synthesized both using polyvinyl alcohol (PVA) aqueous solutions and via solid-state reaction between PVA and boric acid (H_3BO_3), which interacts with polyols such as PVA to form ethers.²

Reacting solid PVA and boric acid at 200–250 °C creates B–O–C bonds. After heating in air at 700–800 °C for 120 min a product called PVBO is obtained. High-purity boron carbide nanopowder with plate-like particles was obtained by its thermal reduction in an argon atmosphere at 1475 °C.³ Boron carbide nanoparticles and nanorods have been synthesized;⁴ and dry mixtures reacted *in vacuo* at 200–250 °C.⁵ From the C: B_2O_3 molar ratio and X-ray diffraction (XRD) the optimum PVA: H_3BO_3 ratio, temperature and holding time have been found

¹ Chkhartishvili, L., Mikeladze, A., Tsagareishvili, O., Gachechiladze, A., Oakley, A. & Margiev, B. Boron-containing nanocrystalline ceramic and metal–ceramic materials. In: *Handbook of Nanomaterials for Industrial Applications* (ed. Ch.M. Hussain), pp. 13–35. Amsterdam: Elsevier (2018).

² Pappin, B., Kiefel, M.J. & Houston, T.A. Boron–carbohydrate interactions. In: *Carbohydrates—Comprehensive Studies on Glycobiology and Glycotechnology* (ed Ch.-F. Chang), ch. 3. Intech Open (2012).

³ Shawgi, N., Li, S.X. & Wang, S. Novel method of synthesis of high purity nano plated boron carbide powder by a solid-state reaction of poly (vinyl alcohol) and boric acid. *Ceram. Intl* **43** (2017) 10554–10558.

⁴ Shawgi, N., Li, S.X., Wang, S., Li, Y. & Ramzi, R. An innovative method of synthesis of nanoparticles and rod-like shape boron carbide by a solid-state polymerization (SSP) of poly (vinyl alcohol) and boric acid. *Ceram. Intl* **44** (2018) 9887–9892.

⁵ Shawgi, N., Li, S.X., Wang, S., Li, Y. & Ramzi, R. Towards a large-scale production of boron carbide nano particles from poly (vinyl alcohol) and boric acid by a solid-state reaction-pyrolysis process (SRPP). *Ceram. Intl* **44** (2018) 774–778.

to be 3.5–3.7, 600 °C and 2 h, respectively.⁶ PVBO gel was synthesized by mixing PVA and H_3BO_3 solutions (molar ratio 4.2:1) and evaporating the water.⁷ After heating in air at 450–700 °C for 2 h, it was ground and gradually heated up at 1100–1300 °C for 5 h at a rate of 10 °C/min in flowing argon. Boric acid ethers made with other organic compounds have also been used to obtain boron carbide powders.^{8–14}

A low-temperature synthesis of boron carbide powder via carbothermal reduction was realized using a condensed product prepared from boric acid and polyols such as glycerol and mannitol as well as PVA.¹⁵ Thermal decomposition in air of the product adjusted the amount of carbon to the stoichiometric $\text{C}:\text{B}_2\text{O}_3$ ratio required for carbothermal reduction. The improved dispersibility and homogeneity of the $\text{B}_2\text{O}_3/\text{C}$ microstructure accelerated B_4C formation at the lower temperature: crystalline B_4C powder with little free carbon was synthesized by such heat treatment at a relatively low temperature of 1200 °C in argon flow. This was applied to the synthesis of powders of other boron compounds (boron nitride and calcium hexaboride). Modified starch and boron oxide were used to obtain doped powdered B_4C and a B_4C –SiC composite.¹⁶ Saccharides have also been used as the carbon source for the carbothermal synthesis of boron carbide,^{17–23} and cellulose, to synthesize fine uniform B_4C particles.²⁴

⁶ Murray, P. *Low Temperature Synthesis of Boron Carbide Using a Polymer Precursor Powder Route*. PhD thesis, University of Birmingham, England (2011).

⁷ Yanase, I., Ogawara, R. & Kobayashi, H. Synthesis of boron carbide powder from polyvinyl borate precursor. *Mater. Lett.* **63** (2009) 91–93.

⁸ Suri, A.K., Subramanian, C., Sonber, J.K. & Murthy, T.S.R.C. Synthesis and consolidation of boron carbide: A review. *Intl Mater. Rev.* **55** (2010) 4–40.

⁹ Sinha, A., Mahata, T. & Sharma B.P. Carbothermal route for preparation of boron carbide powders from boric acid–citric acid gel precursor. *J. Nucl. Mater.* **301** (2002) 165–169.

¹⁰ Barros, P.M., Valeria, I., Yoshida, P. & Schiavon, M.A. Boron-containing poly (vinyl alcohol) as ceramic precursor. *J. Non-Cryst. Solids* **352** (2006) 3444–3450.

¹¹ Kakiage, M., Tahara, N., Yanagidani, S., Yanase, I. & Kobayashi, H. Effect of boron oxide/carbide arrangement of precursor derived from condensed polymer–boric acid product on low-temperature synthesis of boron carbide powder. *J. Ceram. Soc. Jpn* **119** (2011) 422–425.

¹² Kakiage, M., Tahara, N., Yanase, I. & Kobayashi, H. Low-temperature synthesis of boron carbide powder from condensed boric acid–glycerine product. *Mater. Lett.* **65** (2011) 1839–1841.

¹³ Kakiage, M., Tominaga, Y., Yanase, I. & Kobayashi, H. Synthesis of boron carbide powder in relation to composition and structural homogeneity of precursor using condensed boric acid–polyol product. *Powder Technol.* **221** (2012) 257–263.

¹⁴ Tahara, N., Kakiage, M., Yanase, I. & Kobayashi, H. Effect of addition of tartaric acid on synthesis of boron carbide powder from condensed boric acid–glycerin product. *J. Alloys Composites* **573** (2013) 58–64.

¹⁵ Kakiage, M. Low-temperature synthesis of boride powders by controlling microstructure in precursor using organic compounds. *J. Ceram. Soc. Jpn* **126** (2018) 602–608.

¹⁶ Chang, I.T.H. & Falticeanu, C.L. Production of boron carbide powder. US Patent Application 2015/0299421A1.

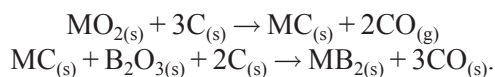
¹⁷ Maqbool, M., Din, R. Zahid, G.H., Ahmad, E., Asghar, Z., Subhani, T., Shahzad, M. & Kaleem, I. Effect of saccharides as carbon source on the synthesis and morphology of B_4C fine particles from carbothermal synthesis precursors. *Mater. Express* **5** (2015) 390–400.

¹⁸ Pilladi, T.R., Ananthasivan, K. & Anthonysamy, S. Synthesis of boron carbide from boric oxide–sucrose gel precursor. *Powder Technol.* **246** (2012) 247–251.

¹⁹ Pilladi, T.R., Ananthasivan, K., Anthonysamy, S. & Ganesan, V. Synthesis of nanocrystalline boron carbide from boric acid–sucrose gel precursor. *J. Mater. Sci.* **47** (2012) 1710–1718.

2.2 Synthesis of MB₂ powders

The first stage of synthesis of borides is the production of metal carbides, and then their boronizing:



Let us consider zirconium diboride (ZrB₂) powders from hybrid organic–inorganic precursors, starting from boric acid and zirconium oxychloride octahydrate, alkoxides, oxide, diketonates, carboxylates, etc. Preceramic precursors contain the ZrO₂–B₂O₃–C system. In the case using zirconium oxide without the intermediate carbide formation reaction, the reaction is:



The sol–gel method is often used to obtain borides with varied functional properties. For example, from the system zirconium oxychloride octahydrate–boric acid–sucrose–citric acid–ammonium hydroxide–polyvinyl alcohol, ZrB₂ precursor films are obtained, high temperature pyrolysis of which gives ceramic films.²⁵ This method is also carried out using water-soluble oligomers and polymers. It was found that the morphology of the ZrB₂ particles depends on gelation temperature, amount of water, and ethylene glycol.²⁶ ZrB₂ nanoparticles were synthesized using zirconium *n*-propoxide (Zr(OCH₂CH₂CH₃)₄), boric acid and sucrose (C₁₂H₂₂O₁₁) with acetylacetone used as a zirconium *n*-propoxide hydrolysis modifier (stabilizer). It was established that when the molar ratio of B:Zr is 2.3 at 1550 °C, only the ZrB₂ phase is obtained with an average grain size of about 50 nm.²⁷

Zirconium diboride ultrafine hollow spheres were obtained by a combined sol–gel and borocarbothermal reduction technique. The gel was obtained from zirconium oxychloride octahydrate, boric acid and glucose. Citric acid and ethylene glycol were used as chelating agents. The full reaction is:



Two, monoclinic m-ZrO₂ and tetragonal t-ZrO₂, crystallite phases of ZrO₂ were observed for samples annealed at 1100 °C, but at 1500 °C only a single ZrB₂ phase was present with a crystallite size of 100–500 nm (via the Debye–Scherrer equation).²⁸ Boric acid reacts quickly

²⁰ Watts, J. *Controlled Synthesis of Boron Carbide Using Solution-Based Techniques*. PhD thesis. Queensland University of Technology, Brisbane (2018).

²¹ Watts, J.L., Talbot, P.C., Alarco, J.A. & Mackinnon, I.D.R. Morphology control in high yield boron carbide. *Ceram. Intl* **43** (2017) 2650–2657.

²² Vijaya, S.K., Krishnaprabhub, R., Chandramoulia, V. & Anthonysamya, S. Synthesis of nanocrystalline boron carbide by sucrose precursor: Method optimization of process conditions. *Ceram. Intl* **44** (2018) 4676–4684.

²³ Mondal, Sh. & Banthia, A.K. Low-temperature synthetic route for boron carbide. *J. Eur. Ceram. Soc.* **25** (2005) 287–291.

²⁴ Sheng, Y., Li, G., Meng, H., Han, Y., Xu, Y., Wu, J., Xu, J., Sun, Zh., Liu, Y. & Zhang, X. An improved carbothermal process for the synthesis of fine-grained boron carbide microparticles and their photoelectrocatalytic activity. *Ceram. Intl* **44** 1052–1058 (2018).

²⁵ Liu, Y., Geng, R., Cui, Y., Peng, Sh., Chang, X., Han, K. & Yu, M. A novel liquid hybrid precursor method via sol–gel for the preparation of ZrB₂ films. *Mater. Design* **128** (2017) 80–85.

²⁶ Zhang, Y. & Sun, H. Effects of gelation temperature, water, polyethylene glycol on morphology of ZrB₂ particles synthesized by sol–gel method. *J. Ceram. Proc. Res.* **19** (2018) 355–359.

²⁷ Li, R., Zhang, Y., Lou, H., Li, J. & Feng, Z. Synthesis of ZrB₂ nanoparticles by sol–gel method. *J. Sol–Gel Sci. Technol.* **58** (2011) 580–585.

²⁸ Cao, Y.-N., Du, S., Wang, J.-K., Zhang, H., Li, F.-L., Lu, L.-L., Zhang Sh.-W. & Deng, X.-G.

with hydroxyl groups. From zirconium oxychloride, boric acid and mannitol a gel was obtained at the relatively low temperature of 1350 °C, annealing of which for 1 h produced the ZrB_2 phase with particles of 200–300 nm.²⁹ In the preceramic precursor the molar ratios were B:Zr = 2.3 and C:Zr = 6.6.

Metal alkoxides are often used to obtain ceramic powder composites that are easily hydrolysed in acid or basic conditions and easily react with chelating compounds. This property of metal alkoxides (e.g., zirconium *n*-propoxide and tantalum ethoxide) was used to obtain ZrB_2 and $\text{ZrB}_2\text{--TaB}_2$. First alkoxides are transformed with 2,4-pentanedione into diketonates and as a result of their hydrolysis a clear solution was obtained. Then a mixture of boric acid solution and phenol–formaldehyde resin was added. After solvent removal by pyrolysis at 1150–1800 °C for 2 h in argon, preceramic powder with spherical particles of 200–600 nm (C:Zr = 4.8 and B:Zr = 3.0) was obtained. Borides were formed by further carbothermal reduction (at 1150–1800 °C for 2 h in argon). Composite powders: $\text{ZrB}_2/\text{B}_4\text{C}$, $\text{ZrB}_2/\text{TaB}_2$, $\text{ZrB}_2/\text{TaB}_2/\text{B}_4\text{C}$, and $\text{ZrB}_2/\text{TaSi}_2$ were also synthesized.³⁰

Inorganic–organic hybrid precursors are also obtained by the interaction of zirconium oxychloride $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, boric acid, and phenolic resin and pyrolysis at 1500 °C; the resulting powder has an average crystallite size of 200 nm, a specific surface area of $\sim 32 \text{ m}^2/\text{g}$ and a low oxygen content ($< 1.0 \text{ wt}\%$).³¹

In the above methods, three major components are required to obtain ZrB_2 : sources of boron, carbon, and zirconium. Borides can also be obtained by two-component systems:³² TiB_2 and ZrB_2 were obtained by the interaction of an organoboron polymer and metal oxides (at 1450 °C for 21 h). Zirconium boride was also electrosynthesized from cryolite–alumina melts containing oxides of zirconium and boron.³³

2.3 Joint synthesis of B_4C and MB_2 component powders

The heating of B_4C –YTZP (yttria-stabilized zirconia polycrystals) mixtures (in argon at 1500 °C) generates B_4C – ZrB_2 composites.³⁴ Composites derived from mixtures that include $\geq 15\%$ YTZP are better sintered than monolithic B_4C fired under the same conditions. Mixtures that include 30% YTZP allow a fired density of $\geq 97.5\%$ theoretical density to be attained. The behaviour of the B_4C –YTZP system is similar to that of the B_4C – TiO_2 system.

Preparation of zirconium diboride ultrafine hollow spheres by a combined sol–gel and boro/carbothermal reduction technique. *J. Sol–Gel Sci. Technol.* **72** (2014) 130–136.

²⁹ Yin, T., Jiang, B., Su, Zh. & Huang, Q. Effects of mannitol on the synthesis of ultra-fine ZrB_2 powders. *J. Sol–Gel Sci. Technol.* **85** (2018) 41–47.

³⁰ Xie, Y., Sanders, T.H. & Speyer, R.F. Solution-based synthesis of submicrometer ZrB_2 and $\text{ZrB}_2\text{--TaB}_2$. *J. Am. Ceram. Soc.* **91** (2008) 1469–1474.

³¹ Yan, Y., Huang, Z., Dong, S. & Jiang, D. New route to synthesize ultra-fine zirconium diboride powders using inorganic–organic hybrid precursors. *J. Am. Ceram. Soc.* **89** (2006) 3585–3588.

³² Su, K. & Sneddon, L.G. A polymer precursor route to metal borides. *Chem. Mater.* **5** (1993) 1659–1668.

³³ Devyatkin, S.V. Electrosynthesis of zirconium boride from cryolite–alumina melts containing zirconium and boron oxides. *Russ. J. Electrochem.* **37** (2001) 1308–1311.

³⁴ Goldstein, A., Geffen, Y. & Goldenberg, A. Boron carbide–zirconium boride *in situ* composites by the reacting pressureless sintering of boron carbide–zirconia mixtures. *J. Am. Ceram. Soc.* **84** (2001) 642–644.

The effect of TiB_2 addition on sintering behavior and mechanical properties of pressureless-sintered B_4C ceramic was studied.³⁵ Addition of 30wt% TiB_2 and sintering at 2150 °C improved the density to about 99% of theoretical. But, as the amount of TiB_2 was increased further, the mechanical properties were degraded.

The effect of TiB_2 addition on sinterability and mechanical properties of B_4C material was investigated.³⁶ addition of TiB_2 permits pressureless sintering at temperatures between 2050 and 2150 °C. This also alleviates grain growth during sintering. 98.5% of theoretical density is reached by increasing the percentage of TiB_2 .

B_4C -nano TiB_2 composite powder was produced by a chemical method.³⁷ Starting materials were boron carbide, carbon, and titanium(IV) isopropoxide (TTIP). TTIP was hydrolysed to produce $\text{Ti}(\text{OH})_4$, which by heat-treatment transforms first into TiO_2 and then TiB_2 . It was found that heat-treatment time and temperature have significant effects on the amount and size of the TiB_2 powder. The data also revealed that the minimum temperature for TiB_2 formation is 650 °C.

Boron carbide matrix composites containing B_4C - TiB_2 (10–40vol.%) were fabricated *in situ* via chemical reaction of B_4C , TiO_2 , and graphite powders at 2050 °C and 35 MPa.³⁸ Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showed that the submicron/nano-sized TiB_2 particles are uniformly located within the matrix grains and at the B_4C grain boundaries. Fracture toughness had a maximum value of 8.2 MPa $\text{m}^{1/2}$ for the 40vol.% B_4C - TiB_2 composite. The main toughening mechanisms are microcrack toughening and crack deflexion toughening.

An additive reinforcing phase and sintering aids were used to improve sinterability:³⁹ B_4C composite with 10vol.% of TiB_2 nanoparticles and 1.5 or 2.5vol.% iron or nickel, respectively, was mixed in an isopropanol environment containing tungsten carbide pellets. After drying, the obtained mixture was formed by cold pressing and the parts sintered at 2400 °C. Addition of Fe and Ni improved density, hardness, Young's modulus and fracture toughness, with Ni addition especially increasing them. SEM showed the arrangement of the additives: FeB and Ni_3B blades were observed. If the boron carbide contained 5.0wt% phenolic resin as a carbon source, the B_4C -nano TiB_2 composite powder could be obtained at temperatures higher than 1250 °C.⁴⁰

Hydrolysis of titanium tetraisopropanol was performed using a surface-active substance (Triton X-100).⁴¹ Heat-treatment of boron carbide-containing gel leads to the formation of

³⁵ Baharvandi, H.R., Hadian, A.M. & Alizadeh, A. Processing and mechanical properties of boron carbide–titanium diboride ceramic matrix composites. *Appl. Composite Mater.* **13** (2006) 191–198.

³⁶ Baharvandi, H.R. & Hadian, A.M. Pressureless sintering of TiB_2 - B_4C ceramic matrix composite. *J. Mater. Engng Performance* **17** (2008) 838–841.

³⁷ Baharvandi, H., Talebzadeh, N., Ehsani, N. & Aghand, F. Synthesis of B_4C -nano TiB_2 composite powder by sol–gel method. *J. Mater. Engng Performance* **18** (2009) 273–277.

³⁸ Wang, Y.-J., Peng, H.-X., Ye, F. & Zhou, Y. Effect of TiB_2 content on microstructure and mechanical properties of *in situ* fabricated $\text{TiB}_2/\text{B}_4\text{C}$ composites. *Trans. Nonferrous Met. Soc. China* **21** (2011) s369–s373.

³⁹ Lati, H., Moradkhani, A., Baharvandi, H. & Martikainen, J. Fracture toughness determination and microstructure investigation of a B_4C -nano TiB_2 composite with various volume percent of Fe and Ni additives. *Mater. Design* **62** (2014) 392–400.

⁴⁰ Khorrami, S.A., Baharvandi, H.R. & Lotfi, R. The effect of calcination temperature on synthesis of B_4C -nano TiB_2 composite by co-precipitation method. *Orient. J. Chem.* **32** (2016) 2243–2249.

⁴¹ Khorrami, S.A., Lotfi, R. & Moradi, Sh. Surfactant effect on the synthesis of B_4C -nano TiB_2 composite by co-precipitation method. *J. Appl. Chem. Res.* **10** (2016) 7–13.

B₄C–nano TiB₂ composites containing 10wt% TiB₂. The sizes of TiB₂ nanoparticles on B₄C were 10–82 and 20–35 nm without and with surfactant, respectively.

B₄C–TiB₂ composites were fabricated via reaction hot pressing at 2100 °C and 25 MPa using B₄C and Ti₃SiC₂ powders as raw materials.⁴² It was found that SiC and TiB₂ particles are homogenously dispersed in the B₄C–TiB₂ composites; TiB₂ nanoparticles are mainly located within the B₄C grains while the larger TiB₂ particles are at the grain boundaries. Due to the pinning effect of SiC and TiB₂ particles on B₄C grain growth, the grain size of the composite was significantly reduced, leading to a great improvement of the mechanical properties. B₄C–TiB₂ composite prepared from B₄C–10wt% Ti₃SiC₂ starting powder shows high flexural strength, fracture toughness and microhardness of 592 MPa, 7.01 MPa m^{1/2}, and 3163 kg/mm², respectively.

Boron carbide and reactor grade zirconium oxide were used to prepare a dense B₄C–ZrB₂ composite.⁴³ 95wt% B₄C and 5wt% ZrO₂ powders were turbo-mixed for 4 h. Reactive hot pressing was at 1800 °C for 1 h with a pressure of 30 MPa under a vacuum of 10^{−5} mbar.

3. Novel technologies

Here, we try to answer how to combine the methods of obtaining boron carbide, titanium and zirconium diborides in a single technological cycle in order to obtain powder ceramic composites B₄C–TiB₂ and B₄C–ZrB₂.

Earlier, our research found the possibility of creating the same composite from either amorphous boron and TiO₂–glycerol–H₂O or H₃BO₃–TiO₂–glycerol–H₂O,^{44–47} obtaining a nanoscale powder B₄C–TiB₂ composite at moderate temperatures.

From §2 we conclude that in the synthesis of metal (titanium and zirconium) diborides, organic compounds of different classes are often used. Amorphous boron, boron oxide, boric acid and its derivatives, boron halides and bororganic compounds are used as boron sources. From a commercial point of view, it is better to use cheaply available compounds (B₂O₃, H₃BO₃ and B(OR)₃).

The sol–gel and coprecipitation methods are often used to obtain precursors and preceramic powders of metal borides and boron carbides. The comparison of the two main approaches (Schemes 1 and 2) of obtaining boron carbide and metal diborides shows that the final products are obtained using actually the same technological processes.

⁴² He, P., Dong, Sh., Kan, Y., Zhang, X. & Ding, Y. Microstructure and mechanical properties of B₄C–TiB₂ composites prepared by reaction hot pressing using Ti₃SiC₂ as additive. *Ceram. Intl* **42** (2016) 650–656.

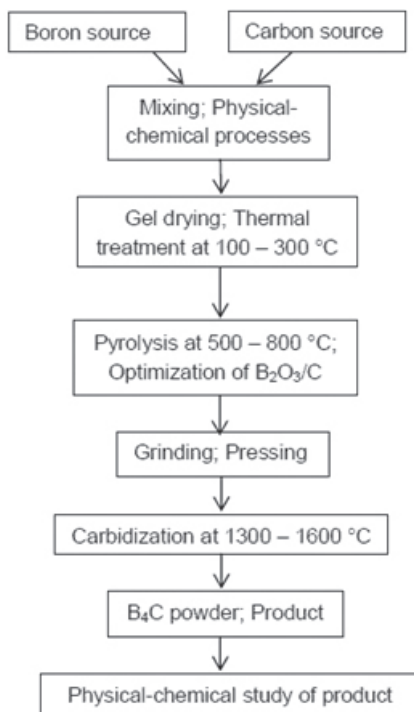
⁴³ Murthy, T.S.R.Ch., Ankata, S., Sonber, J.K., Sairam, K., Singh, K., Nagaraj, A., Sengupta, P., Bedse, R.D., Majumdar, S. & Kain, V. Microstructure, thermo-physical, mechanical and wear properties of *in-situ* formed boron carbide–zirconium diboride composite. *Ceramics Silicates* **62** (2018) 15–30.

⁴⁴ ISTC Project # G–462: *New Hard Alloys with Nanocrystalline Components* (2001–2003).

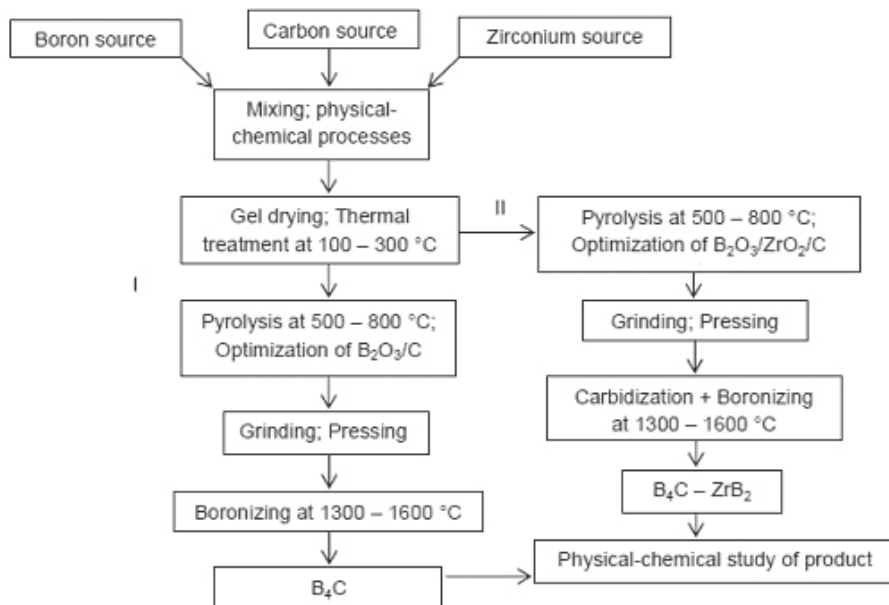
⁴⁵ STCU Project # 4600: *Tungsten, Titanium, and Boron Carbide-Based Nanocrystalline Hardmetals* (2009–2011).

⁴⁶ Tsagareishvili, O., Mikeladze, A., Chedia, R. & Chkhartishvili, L. Method of obtaining boron carbide based hard nanocomposite materials. *National Centre for Intellectual Property of Georgia “Geo Patent”*—Patent # GE P2018 6709 B.

⁴⁷ Mikeladze, A., Tsagareishvili, O., Chkhartishvili, L., Chedia, R. & Darchiashvili, M. Production of titanium-containing metal-ceramic composites based on boron carbide in the nanocrystalline state. *Adv. Appl. Ceram.: Structure Function Bioceram.* **118** (2019) 196–208.



Scheme 1. General view of technological route for obtaining boron carbide when using organic compounds as carbon sources.



Scheme 2. General view of technological route of obtaining of B_4C and B_4C-ZrB_2 when using organic compounds as carbon sources.

For example, sources of boron, zirconium, and carbon are necessary for obtaining zirconium diboride and in this case route I in Scheme 2 needs to be implemented. The main problem is optimization of the $\text{B}_2\text{O}_3\text{:ZrO}_2\text{:C}$ ratio during pyrolysis, especially ensuring removal of excess carbon; the optimal temperature is 500–800 °C depending on the nature of the organic compound. With carbohydrates, pyrolysis is achieved up to 500 °C. With carbon-chain polymers, 700–800 °C is sufficient to form active carbon.

For the preparation of $\text{B}_4\text{C-ZrB}_2$ or $\text{B}_4\text{C-TiB}_2$ composites, boron, zirconium and carbon-containing compounds are also necessary. These composites are mainly obtained by mixing the preprepared powders of borides or letting the appropriate oxides and boron carbides interact. As shown in Scheme 2, route II, it is possible to obtain a composite $\text{B}_4\text{C-ZrB}_2$ (or $\text{B}_4\text{C-TiB}_2$) from the same initial compounds that are necessary to obtain ZrB_2 (or TiB_2). The only difference is the $\text{B}_2\text{O}_3\text{:ZrO}_2\text{:C}$ molar ratio changes in such a way to obtain boron carbide and metal diborides.

Our preliminary studies have established the reality of the implementation of this technological route. For this purpose we have used different composition systems: amorphous boron–PVA– H_2O , amorphous boron–sucrose– H_2O , amorphous boron–PVA– $\text{ZrO}_2\text{-H}_2\text{O}$, $\text{H}_3\text{BO}_3\text{-PVA-TiO}_2\text{-H}_2\text{O}$, $\text{H}_3\text{BO}_3\text{-sucrose-ZrO}_2\text{-H}_2\text{O}$, $\text{H}_3\text{BO}_3\text{-sucrose-TiO}_2\text{-H}_2\text{O}$, $\text{H}_3\text{BO}_3\text{-sucrose-Zr(OR)}_4\text{-propanol-H}_2\text{O}$, $\text{H}_3\text{BO}_3\text{-PVA-Zr(OR)}_4\text{-propanol-H}_2\text{O}$, $\text{H}_3\text{BO}_3\text{-PVA-Ti(OR)}_4\text{-propanol-H}_2\text{O}$, etc.

3.1 Obtaining powder precursors of boron carbide

120 mL water and 25 g sucrose were placed in a porcelain cup. The resulting solution was heat-treated at 90–100 °C and under stirring 31 g of boric acid was added in portions until complete dissolution. Various compounds should be formed (e.g. esters). Water was removed (at ~ 90 °C) under stirring and a viscous mass obtained. Then the temperature was raised to 145–150 °C and maintained until the formation of a black porous mass (within 2 h). The porous mass was cooled and ground in a porcelain mortar. A black powder was obtained with particle size < 1 mm.

40.8 g of powdered sample was placed into quartz pipe under argon or nitrogen and heated up to 550–600 °C. During pyrolysis the following processes occur: sucrose melting (at 185 °C) and intensive destruction (starting from > 226 °C). Up to 324 °C, 30% of the initial mass was left and mass loss at 500 °C was 80%. The resulting boron oxide melted (at 450 °C) and became homogenously distributed in the resulting amorphous carbon matrix. At lower temperature, more amorphous C was obtained than at high temperature (> 600 °C). Pyrolysis lasted 2 h. A weakly sintered large-pored black mass was obtained (Fig. 1), easily ground in a mortar or ball mill. 28.8 g of preceramic mass was obtained. That powder was pressed (40–50 MPa) into tablets and carbidized at 1200–1600 °C in argon or vacuum for 1–5 h.

3.2 Obtaining boron carbide from amorphous boron and PVA

10 g PVA was dissolved in 100 mL water at 80 °C; 5.4 g of amorphous boron powder (particle size 0.5–1 µm) was added in portions with stirring; the whole was placed into an ultrasonic homogenizer for 30 min. The suspension was placed into a Teflon bowl and water removed at 150–180 °C. A black fragile mass was obtained (Figs 2–4), which was ground and heated in air

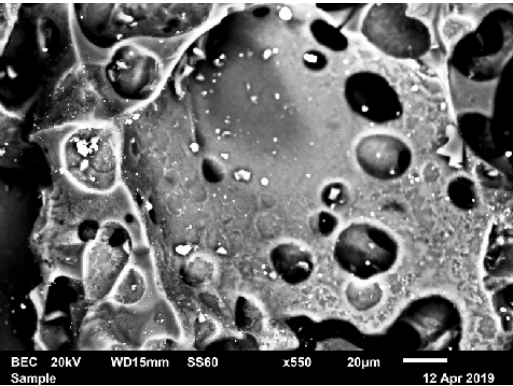


Figure 1. SEM image of pyrolysed B₄C precursors.

at 300 °C for 1 h and then at 700 °C in an argon stream for 2 h. Approximately 17.5 g of the preceramic mass was obtained, which was ball-milled, pressed at 40–50 MPa into tablets and carbidized at 1200–1600 °C in argon or vacuum for 1–5 h.

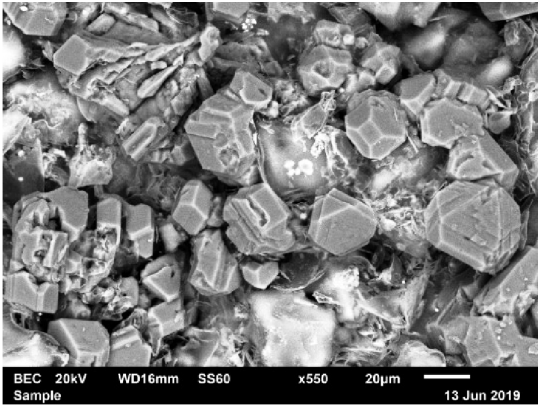


Figure 2. SEM image of synthesized B₄C.

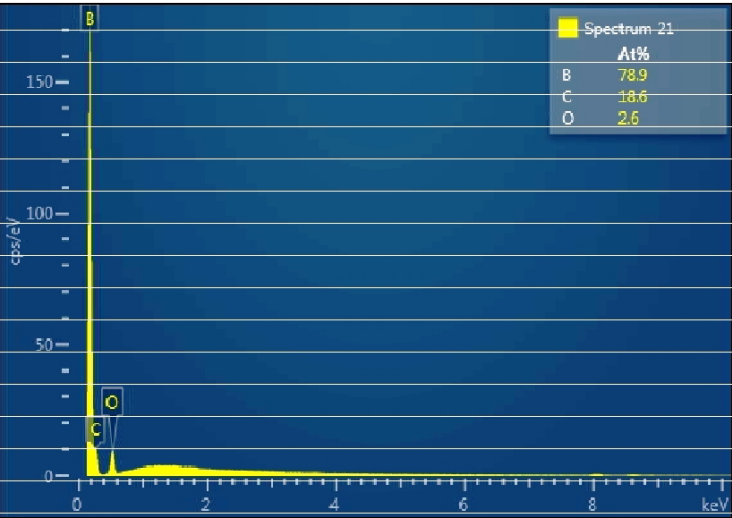


Figure 3. EDX spectrum of synthesized B₄C.

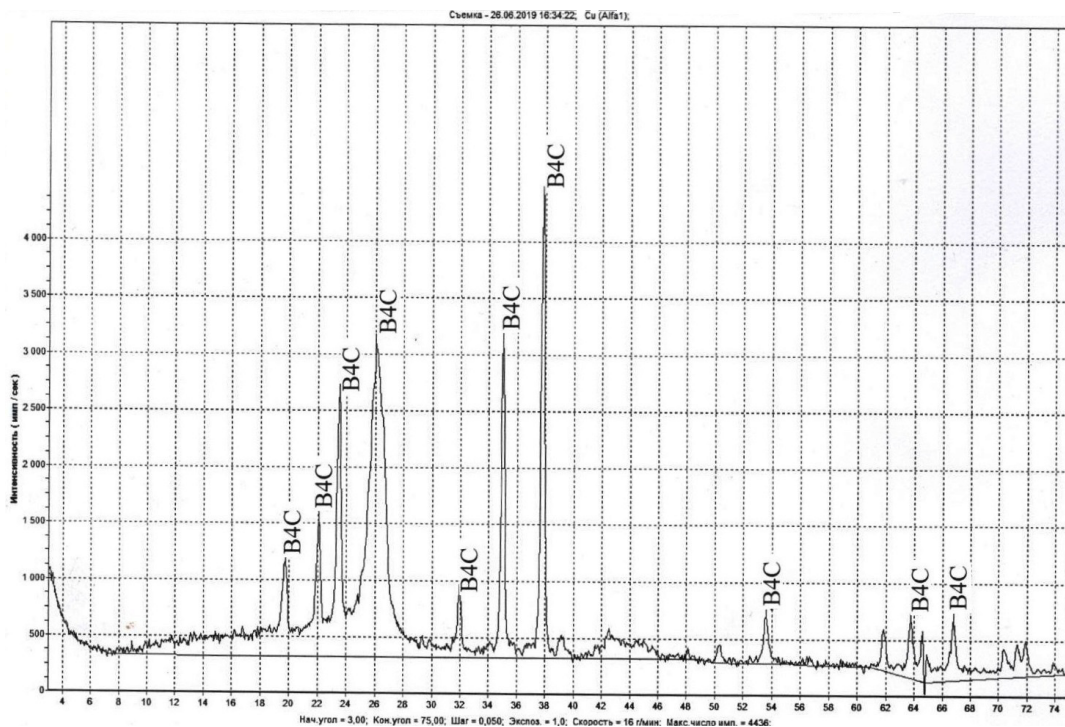


Figure 4. XRD spectrum of synthesized B_4C .

Ceramic powder composite precursors of B_4C –20% ZrB_2 and B_4C –20% TiB_2 were obtained similarly, but the concentration of PVA in the solution was 5–6% and ultradisperse powders of ZrO_2 and TiO_2 prehomogenized in 10 mL water were added at 80 °C.

3.3 Synthesis of precursors of powder composites B_4C – ZrB_2 and B_4C – TiB_2 by spray-drying method

The spray-drying method is widely used to obtain powders of many functional organic and inorganic materials. Formation of powders of boron carbide-based ceramic composites (and pure boron carbide itself) from aqueous solutions by this method is easy and cheap.

Precursor powders were prepared using the methods described above, as suspensions by adding titanium or zirconium oxides to boric acid–carbohydrate (sucrose, glucose, etc.) aqueous solutions at room temperature. It should be taken into account that the solubility of boric acid in water at 25 °C is 5.7 g/100 mL and to increase it 5–10% alcohols or ethanolamines can be added. When PVA is used as the carbon source, its solution concentration was 2–3%.

A laboratory spray-drying apparatus was constructed with a 10 L titanium chamber and had the following characteristics: throughput 5–20 mL/min, chamber temperature 100–300 °C, air pressure during spraying 1.1–1.5 atm.

The powder obtained by spray-drying was collected into a cyclone, sieved, and annealed at 500–600 °C to remove excess free carbon. Carbidization was at 1200–1600 °C in vacuum or an argon atmosphere for 1–5 h.

3.4 Synthesis of precursors of powder composites B_4C – ZrB_2 and B_4C – TiB_2

Synthesis of B_4C –20% ZrB_2 ceramic composite was carried out in several ways; in particular, 120 mL of an aqueous solution containing 27 g sugar was prepared in a porcelain cup or Pyrex glass beaker, heat-treated to 90–100 °C, and to which was added 33 g boric acid in portions under stirring until complete dissolution. Various esters are obtained. 70% of the water was removed at ~90 °C under stirring and a suspension of 2 g of zirconium(IV) oxide (particle size 500–2000 nm) in 10 mL water was added. Homogenization was carried out using a JY92–IIDN ultrasonic homogenizer (20–25 kHz, 600 W) for 20 min. Particle sizes were determined with a Winner 802DLS photon correlation nanoparticle size analyser. After heating at 150 °C for 2 h to remove most of the water, a solid porous black fragile mass (41.7 g) was obtained.

Precursor powder pyrolysis was performed by placing 27 g of powdered simple into the quartz pipe under argon or nitrogen and heating up to 550–600 °C, during which sucrose melting (at 185 °C) and intensive destruction (starting from 226 °C) occur. Up to 324 °C, 30% of the initial mass was left and mass loss at 500 °C was 80%. The boron oxide melted at 450 °C and became homogeneously distributed in the resulting amorphous C matrix. A weakly sintered large-pored black mass was obtained, easily ground. 21.8 g of preceramic mass was obtained (Figs 5 and 6). It was pressed into tablets at 40–50 MPa and carbidized at 1200–1600 °C in argon or vacuum for 1–5 h. Synthesis of B_4C –20% TiB_2 (Fig. 7) was carried out similarly to B_4C –20% ZrB_2 .

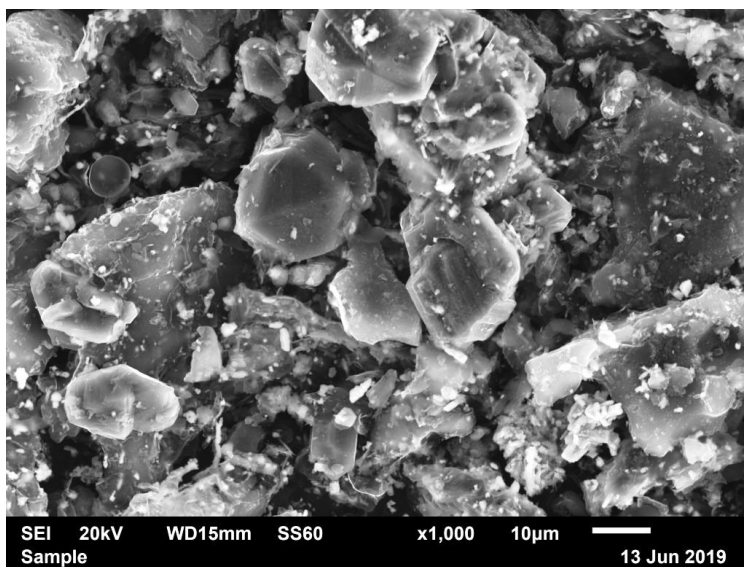


Figure 5. SEM image of synthesized B_4C – ZrB_2 .

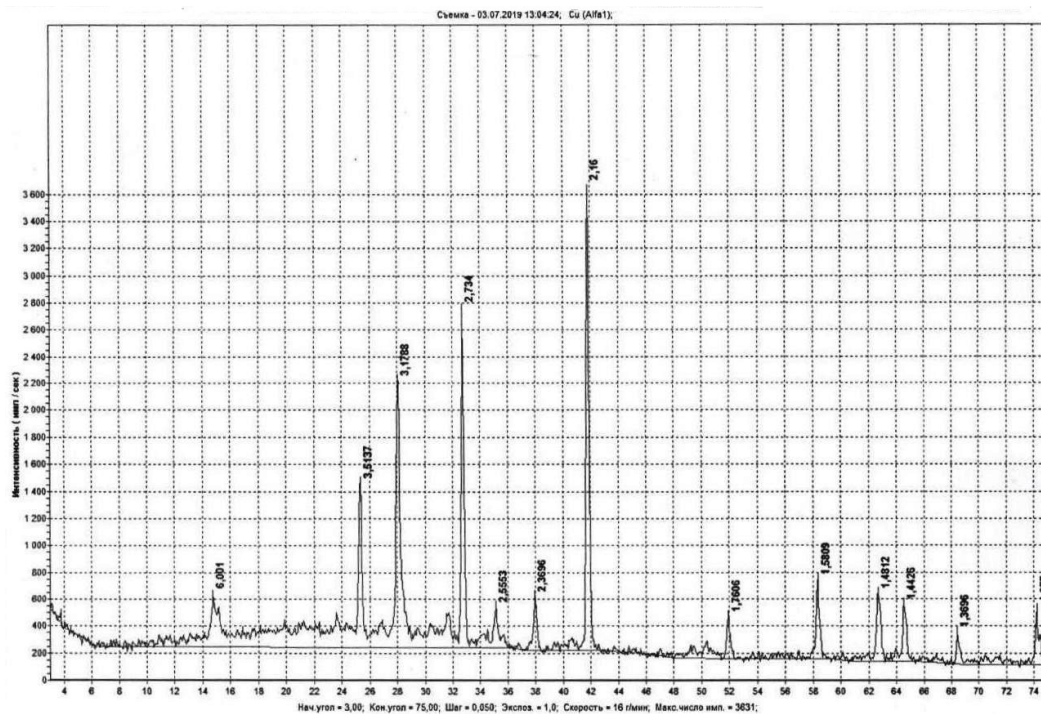


Figure 6. XRD spectrum of synthesized B_4C-ZrB_2 .

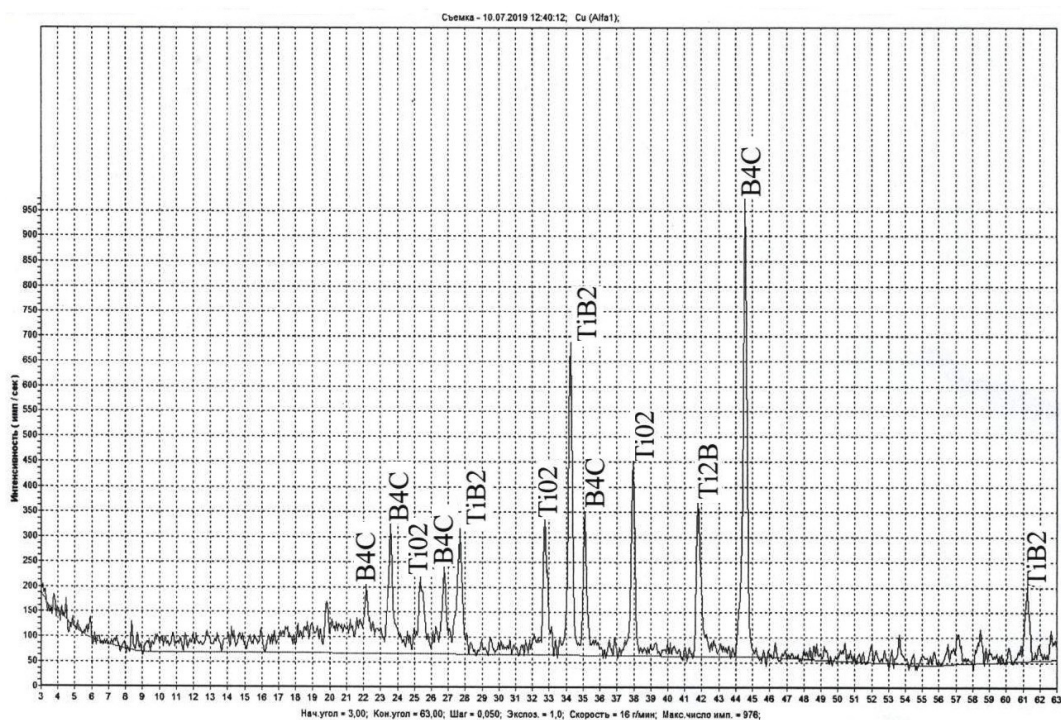


Figure 7. XRD spectrum of synthesized B_4C-TiB_2 .

4. Conclusion

Obtaining ultrafine powders of boron carbide and boron carbide-based nanocomposites using a liquid charge in the form of organic compounds in aqueous solution and suspensions of the inorganic components is highly promising route to develop novel hard materials with advanced mechanical properties.

Acknowledgment

This work was supported by the Shota Rustaveli National Science Foundation of Georgia (SRNSFG)—Grant # AR-18-1045: “Obtaining of boron carbide-based nanostructured heterophase ceramic materials and products with improved performance characteristics”.