

# Adapting of sol–gel process for preparation of $\text{TiB}_2$ powder from low-cost precursors

L. Bača\*, N. Stelzer

*Austrian Research Centers GmbH-ARC, Department of Functional Materials, Surface Engineering Group, Forschungszentrum, A-2444 Seibersdorf, Austria*

Available online 17 October 2007

## Abstract

Sol–gel process has been used for preparation of low-cost titanium diboride ( $\text{TiB}_2$ ) and titanium carbide (TiC) gels and powders. In this process citric acid is used to chelate titanium and boron precursors and ethylene glycol for reaction with this chelate to form organic esters. Thermal behavior of homogeneous gel and relationship between processing parameters and microstructure of powders has been determined. XRD and Raman spectroscopy have been used for a detection of changes during the crystallization. Carbothermal reduction of the gel revealed the formation of  $\text{TiB}_2$  and TiC at 1200 °C for 2 h. Well shaped ball-like TiC crystals with the particle size about 200 nm and hexagonal plate-like  $\text{TiB}_2$  grains with the particle size about 2  $\mu\text{m}$  and thickness 200 nm were formed at 1300 °C for 1 h.

© 2007 Elsevier Ltd. All rights reserved.

**Keywords:** Sol–gel processes; Precursor-organic; Borides; Carbides; Raman spectroscopy

## 1. Introduction

Polycrystalline ceramics based on  $\text{TiB}_2$  have received considerable attention as cutting tools, electrodes for liquid aluminium and wall materials for nuclear fusion.<sup>1</sup>

Commercial methods used for synthesis of  $\text{TiB}_2$  powders are mostly based on high-temperature carbothermic reduction of a mixture of rutile and boric acid. However, this reaction is highly exothermic and needs temperatures above 1800 °C.<sup>2</sup>

By comparison, self-propagating high-temperature synthesis (SHS) has attracted the attention of researchers and companies for manufacturing high-purity  $\text{TiB}_2$  and titanium diboride-based composites.<sup>3–7</sup> The system usually uses powdered metal—magnesium (Mg) or aluminum (Al) and titanium oxide ( $\text{TiO}_2$ ) and boron oxide ( $\text{B}_2\text{O}_3$ ). Another modification of this synthesis is using NaCl as an SHS diluent.<sup>8,9</sup> These materials are mixed and placed into a high-temperature crucible. The mixture is then ignited and the reaction between the two oxides and the metal powder proceeds to completion. Once started, the self-sustaining reaction reaches temperatures of more than 2000 °C.

Submicron and nanocrystalline titanium diboride powder with average particle size less than 200 and 50 nm can be produced by ball-milling a mixture of  $\text{TiO}_2$ ,  $\text{B}_2\text{O}_3$  and Mg metal for 15 and 100 h respectively, as reported by Welham.<sup>10</sup> When a mixture of pure Ti and BN powders has been used, 2 h of high-energy ball-milling has started the reaction to produce TiN and  $\text{TiB}_2$  mixture by displacement reaction. After 16 h of composite powder milling, 10 nm crystallites of TiN and  $\text{TiB}_2$  have been obtained.<sup>11</sup>

Nanocrystalline  $\text{TiB}_2$  with a narrow particle size distribution (~15 nm) has been also prepared by the reduction-boronation method at 400 °C in which boron tribromide ( $\text{BBr}_3$ ) and Ti powder have been used as a source material and metallic sodium as a reductant.<sup>12</sup> The same authors reported a facile one-step route to nanocrystalline  $\text{TiB}_2$  powders by solvothermal reaction of  $\text{TiCl}_4$  with  $\text{NaBH}_4$  in the temperature range of 500–700 °C in an autoclave.<sup>13</sup>

Although ultra-fine  $\text{TiB}_2$  powders and their composites have been successfully synthesized by either high-energy ball-milling or solvothermal route in autoclave, there is still potential in preparation of cheap  $\text{TiB}_2$  powder. In the present study we report for a first time adapted Pechini method for synthesis of nonoxide powders. Low-cost inorganic precursors ( $\text{TiCl}_4$  and  $\text{B}_2\text{O}_3$ ) have been chelated by citric acid and polymerized by ethylene glycol to form polymer-derived ceramic precursor.

\* Corresponding author.

E-mail address: [lubos.baca@arcs.ac.at](mailto:lubos.baca@arcs.ac.at) (L. Bača).

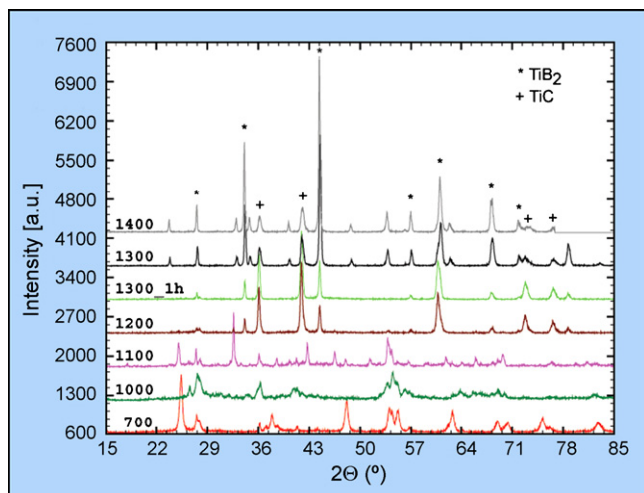
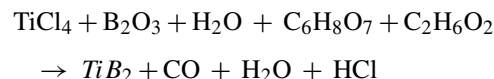


Fig. 1. XRD analysis revealed the sequence in carbothermal reduction of polymer-derived ceramic gels of Ti and B during heat treatment.

## 2. Experimental

Titanium diboride ( $\text{TiB}_2$ ) powder was prepared by carbothermic reduction of stoichiometric mixture of titanium tetrachloride

( $\text{TiCl}_4$ , 99.9%, Acros Organics, Belgium) and boron oxide ( $\text{B}_2\text{O}_3$ , Rio Tinto Borax, CA, USA). Citric acid (CA) was used to chelate with Ti and B precursors by forming a polybasic acid. After homogenization of the solution containing cations, ethylene glycol (EG) was added in CA:EG ratio of 2:3, to promote mixed citrate polymerization. During evaporation of water from system, gelation occurred. Obtained gel was dried at  $180^\circ\text{C}$  for 48 h and crushed prior to heat treatment. Formed organic ester was used as a carbon source. Heat treatment was done in tube furnace at different temperatures in flowing Ar atmosphere. The schematic reaction is suggested as follows:



Phase analysis was conducted and recorded using powder-XRD X-pert (Philips). Field emission scanning electron microscopy (FESEM, Carl Zeiss SUPRA<sup>TM</sup> 40VP) was used to study crystal size and morphology of  $\text{TiB}_2$  powder. EDX spectra were recorded to identify chemistry of different morphologies obtained in samples. Raman spectra were measured with the spectrometer Aramis (Horiba Jobin Yvon) equipped with 532 nm laser.

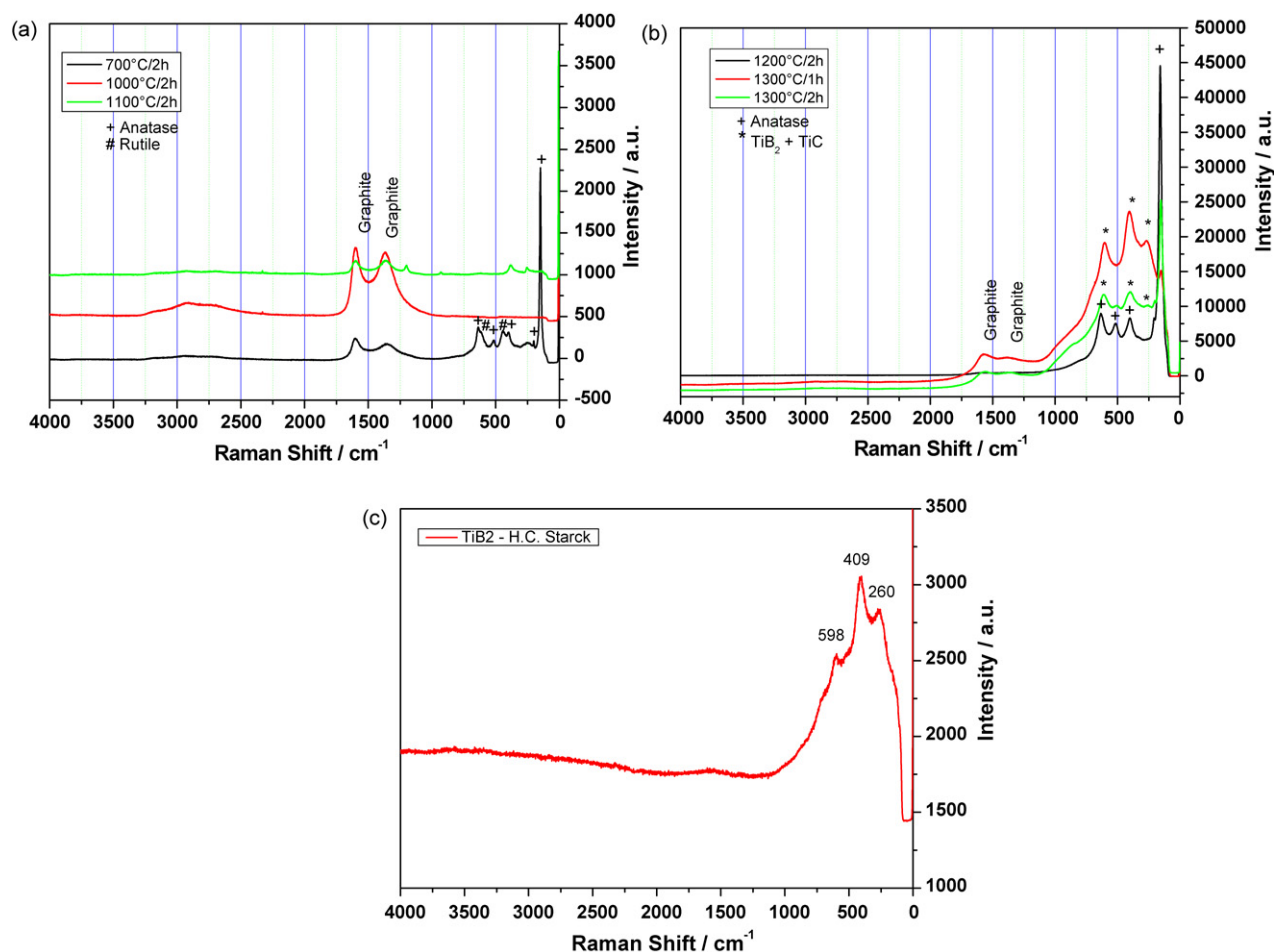


Fig. 2. (a) Raman spectra of polymer-derived ceramic resins obtained by heating at 700, 1000 and 1100 °C for 2 h in flowing argon. (b) Raman spectra of samples already containing  $\text{TiB}_2$  at temperatures of 1200 °C/2 h, 1300 °C/1 h and 1300 °C/2 h. (c) Raman spectra of commercial  $\text{TiB}_2$  powder (H.C. Starck, Germany).

### 3. Results and discussion

#### 3.1. XRD and Raman spectroscopy

The XRD patterns (Fig. 1) of gel samples heated at various temperatures show sequences in  $\text{TiB}_2$  powder evolution. After heat treatment at  $700^\circ\text{C}/2\text{ h}$  only titanium dioxide crystalline phases were formed. As further revealed by Raman spectroscopy (Fig. 2a), these phases were assigned to anatase with bands at

$148, 200, 397, 516$  and  $637\text{ cm}^{-1}$  and rutile at  $445$  and  $611\text{ cm}^{-1}$ . Also Nikolova et al.<sup>14</sup> observed rutile peaks at  $445$  and  $610\text{ cm}^{-1}$  in  $\text{TiC}$  thin film annealed at  $1000^\circ\text{C}$  in an  $\text{H}_2\text{O}/\text{HCl}$  gas mixture.

At  $1000^\circ\text{C}/2\text{ h}$  rutile and carbon were identified together with some very weak unidentified peaks. Raman spectra revealed only major amorphous carbon phase with characteristic bands at  $1368$  and  $1600\text{ cm}^{-1}$ . Lohse et al.<sup>15</sup> recorded the spectra taken from five different particles of the as-received carbon starting powder

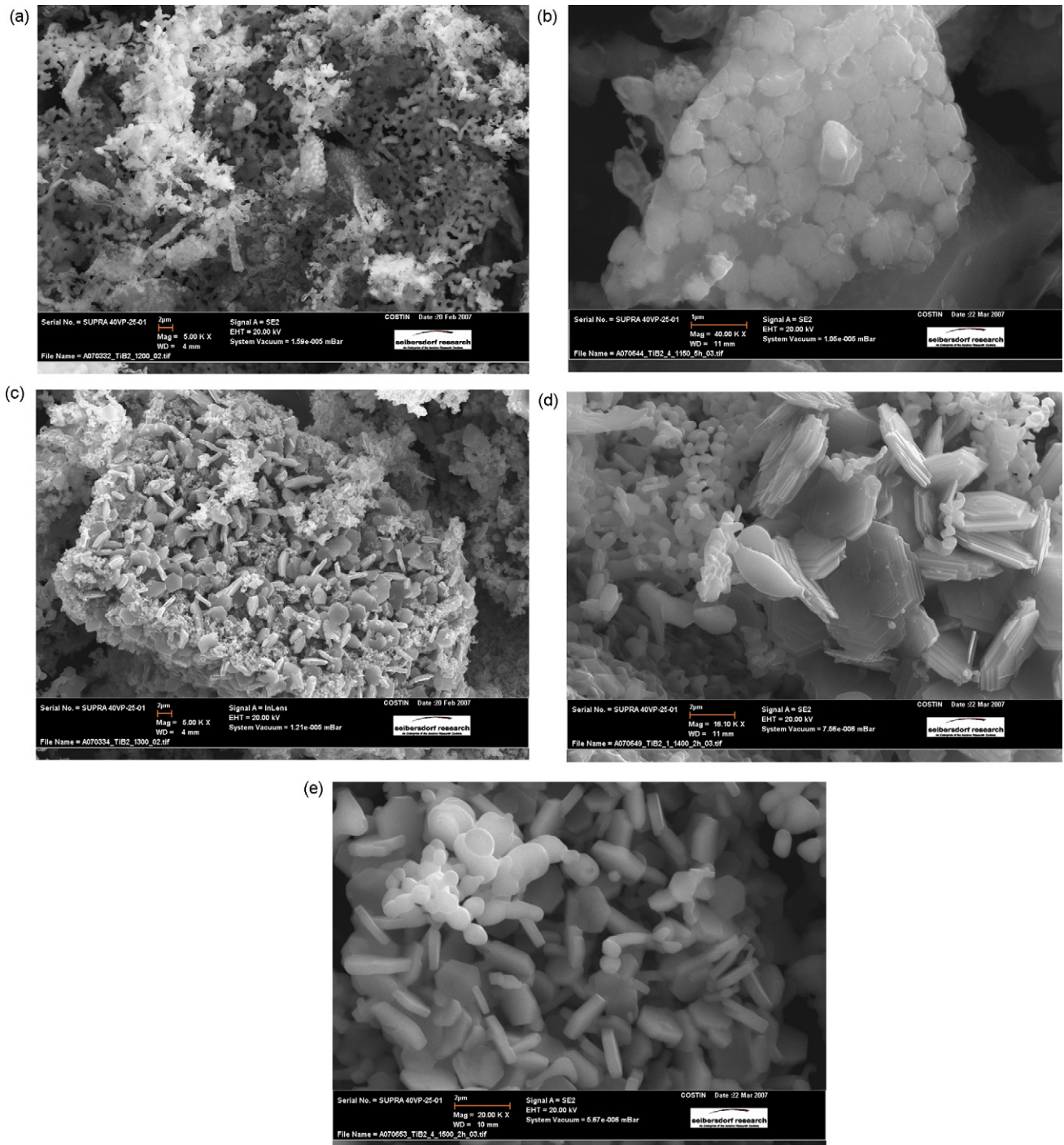


Fig. 3. Scanning electron microscope micrograph of  $\text{TiB}_2$  powder heat treated in flowing Ar atmosphere at: (a)  $1200^\circ\text{C}$  for 2 h, (b)  $1150^\circ\text{C}$  for 5 h, (c)  $1300^\circ\text{C}$  for 2 h, (d)  $1400^\circ\text{C}$  for 2 h and (e)  $1500^\circ\text{C}$  for 2 h.

and they found two strong peaks at approximately 1340 and 1590  $\text{cm}^{-1}$ . These peaks were associated with the A 1g and E 2g vibrational modes of graphite.<sup>16,17</sup>

XRD spectrum at 1100 °C/2 h revealed titanium borate ( $\text{TiBO}_3$ ) as a new phase, the intensity of rutile slightly decreased and the intensity of graphite almost disappeared. Strongly reduced graphite bands were also observed in Raman spectrum. Moreover, very weak new bands at 256, 379, 932 and 1199  $\text{cm}^{-1}$  were observed. These bands could be assigned to new phase identified by XRD as titanium borate.

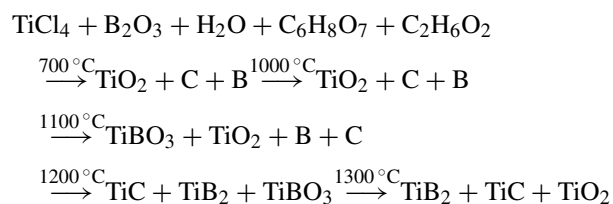
At 1200 °C/2 h the XRD spectrum has been totally changed and titanium carbide (TiC) and titanium boride ( $\text{TiB}_2$ ) appeared. Very weak peak of  $\text{TiO}_2$  was also found. In the Raman spectrum titanium dioxide was identified as anatase phase.

XRD spectrum of sample annealed at 1300 °C for 1 h shows only TiC and  $\text{TiB}_2$  phases without presence of any other phase. However, Raman spectra revealed that small amount of anatase was present also in this sample. Wide bands found at 258, 396 and 610  $\text{cm}^{-1}$  in Raman spectra (Fig. 2b) were assigned to the mixture of  $\text{TiB}_2$  and TiC because of very near distribution of original bands of TiC at 260, 420 and 605  $\text{cm}^{-1}$ <sup>15</sup> and that obtained from the commercial H.C. Starck powder of  $\text{TiB}_2$  at 262, 404, and 598  $\text{cm}^{-1}$  (Fig. 2c). This correlates very well with spectra obtained by XRD.

XRD pattern of samples heated at 1300 °C/2 h and 1400 °C/2 h showed similar phase composition. The intensity of  $\text{TiB}_2$  increased with temperature. The intensity of TiC with temperature decreased while that of  $\text{TiO}_2$  remained unchanged. It is interesting to note that the intensity of anatase at 1200 °C/2 h and 1300 °C/1 h was almost zero and then increased again when the sample was heated at 1300 °C for 2 h. It indicates the preferable reaction between TiC and amorphous B forming  $\text{TiB}_2$  and C at this temperature.

Additionally, new sample was prepared to observe the content of anatase at 1600 °C. XRD spectrum was recorded and revealed that titanium dioxide remained still in  $\text{TiB}_2$ -TiC powder.

Summarizing the results obtained by XRD and Raman spectroscopy the carbothermal reduction of polymer-derived ceramic precursor producing mixed  $\text{TiB}_2$ /TiC powder follows the schematic pathway:



However, boron was not detected by XRD or Raman, due to its amorphous state. According to the scheme boron reacts first with  $\text{TiO}_2$  at 1100 °C to form  $\text{TiBO}_3$ . No other boron based crystalline phase was detected. Pure  $\text{TiB}_2$  powder could not be synthesized from equal molar  $\text{TiCl}_4$  and  $\text{B}_2\text{O}_3$  precursors even at temperature of 1600 °C in protecting argon atmosphere. There were always byproducts of TiC and  $\text{TiO}_2$ .

### 3.2. SEM and EDX analysis

Fig. 3a–e shows the microstructure evolution of polymer derived  $\text{TiB}_2$  precursors heat treated at 1150–1500 °C in flowing argon atmosphere.

At temperature 1200 °C/2 h (Fig. 3a) the morphology of the powder appeared highly porous with formation of necks among the crystals. Crystal size of the synthesized  $\text{TiB}_2$  based powder was about 200 nm, which was agglomerated. However, Fig. 3b shows that crystals of  $\text{TiB}_2$  have a tendency to grow also at lower calcination temperature (1150 °C) during longer soaking time (5 h). The spherical nanoparticles formed pre-sintered clusters. At higher temperatures these oriented clusters formed highly faceted  $\text{TiB}_2$  hexagonal mica-like crystals and spherical TiC particles as shown in Fig. 3c–e. EDX analysis was recorded to distinguish this bimodal morphology of powders (Fig. 4a and b).

In samples prepared at 1500 °C for 2 h mica-like hexagonal crystals were sintered together forming hexagonal single crystals without further evidence of mica-like sheets. Similar morphology of  $\text{TiB}_2$  particles was observed also by Welham<sup>10</sup> after 15 h ball-milling of  $\text{TiO}_2$ ,  $\text{B}_2\text{O}_3$  and Mg powders. The par-

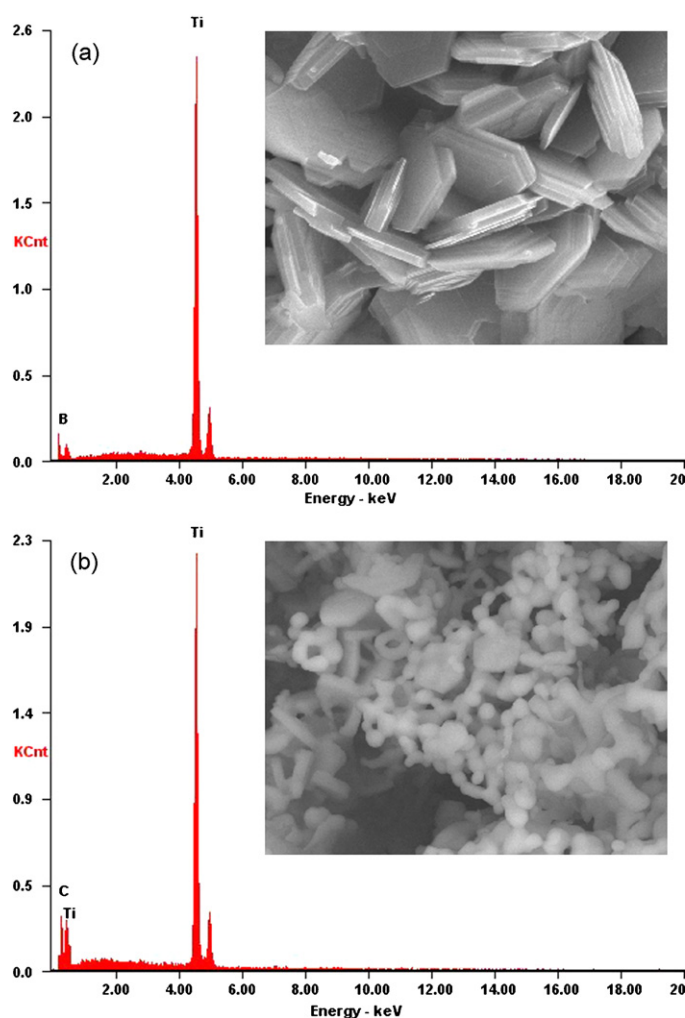


Fig. 4. EDX spectra of sample treated at 1400 °C for 2 h. (a) Spectrum of hexagonal plates revealed presence of Ti and B and (b) spectrum of spherical particles revealed presence of Ti and C.

ticles size of spherical TiC increased from 200 nm at 1300 °C/2 h to 400–500 nm at 1500 °C/2 h.

#### 4. Conclusions

Titanium diboride powder has been successfully synthesized by esterification of Ti and B inorganic precursors followed by heat treatment in argon atmosphere. It was found that byproducts of TiC and TiO<sub>2</sub> were present in the as-synthesized powders even at temperature of 1600 °C for 2 h.

Based on XRD and Raman analysis a reaction scheme was suggested for single steps of carbothermal reduction of Ti and B species prepared from the precursors by this method.

SEM and EDX analysis revealed well shaped hexagonal plate-like TiB<sub>2</sub> crystals with the particle size about 2 μm and thickness 200 nm, and spherical TiC particles with the crystal size about 200 nm prepared at 1300 °C for 1 h.

#### References

1. Padmanabhan, K. R. and Sorensen, G., The effect of ion implantation on R.F. sputtered TiB<sub>2</sub> films. *Thin Solid Films*, 1981, **81**(1), 13–19.
2. Schwartzkopf, P. and Kieffer, R., *Refractory Hard Metals: Borides, Carbides, Nitrides and Silicides*. Macmillan, New York, 1953, p. 447.
3. Miyamoto, Y. and Koizumi, M., High-pressure self-combustion sintering for ceramics. *Com. Am. Ceram. Soc.*, 1984, **11**, C-224–C-225.
4. Tomoshige, R., Murayama, A. and Matsushita, T., Production of TiB<sub>2</sub>–TiN composites by combustion synthesis and their properties. *J. Am. Ceram. Soc.*, 1997, **80**(3), 761–764.
5. Nakane, S., Takano, Y., Yoshinaka, M., Hirota, K. and Yamaguchi, O., Fabrication and mechanical properties of titanium boride ceramics. *J. Am. Ceram. Soc.*, 1999, **82**(6), 1627–1628.
6. Klinger, L., Gotman, I. and Horvitz, D., In situ processing of TiB<sub>2</sub>/TiC ceramic composites by thermal explosion under pressure: experimental study and modeling. *Mater. Sci. Eng.*, 2001, **A302**, 92–99.
7. Weimin, W., Zhengyi, F., Hao, W. and Runzhang, Y., Chemistry reaction processes during combustion synthesis of B<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub>–Mg system. *J. Mater. Proc. Technol.*, 2002, **128**, 162–168.
8. Khanra, A. K., Godkhindi, M. M. and Pathak, L. Ch., Comparative studies on sintering behavior of self-propagating high temperature synthesized ultra-fine titanium diboride powder. *J. Am. Ceram. Soc.*, 2005, **88**(6), 1619–1621.
9. Khanra, A. K., Pathak, L. Ch., Mishra, S. K. and Godkhindi, M. M., Effect of NaCl on the synthesis of TiB<sub>2</sub> powder by self-propagating high-temperature synthesis technique. *Mater. Lett.*, 2004, **58**, 733–738.
10. Welham, N. J., Formation of nanometric TiB<sub>2</sub> from TiO<sub>2</sub>. *J. Am. Ceram. Soc.*, 2000, **83**(5), 1290–1292.
11. Shim, J.-H., Byun, J.-S. and Cho, Y. W., Mechanochemical synthesis of nanocrystalline TiN/TiB<sub>2</sub> composite powder. *Scripta Mater.*, 2002, **47**, 493–497.
12. Chen, L., Gu, Y., Shi, L., Yang, Z., Ma, J. and Qian, Y., A reduction–boronation route to nanocrystalline titanium diboride. *Solid State Commun.*, 2004, **130**, 231–233.
13. Chen, L., Gu, Y., Qian, Y., Shi, L., Yang, Z. and Ma, J., A facile one-step route to nanocrystalline TiB<sub>2</sub> powders. *Mater. Res. Bull.*, 2004, **39**, 609–613.
14. Nikolova, P., Petkov, M., Tinchev, S. and Dyulgarska, J., Conversion of magnetron deposited TiC films into rutile TiO<sub>2</sub>. *Plasma Processes Polym.*, 2006, **3**(2), 188–191.
15. Lohse, B. H., Calka, A. and Wexler, D., Raman spectroscopy as a tool to study TiC formation during controlled ball milling. *J. Appl. Phys.*, 2005, **97**, 114912.
16. Amer, M., Barsoum, M. W., El-Raghy, T., Weiss, I., Leclair, S. and Lip-tak, D., The Raman spectrum of Ti<sub>3</sub>SiC<sub>2</sub>. *J. Appl. Phys.*, 1998, **84**(10), 5817–5819.
17. Rao, J., Cruz, R., Lawson, K. J. and Nicholls, J. R., Sputtered DLC–TiB<sub>2</sub> multilayer films for tribological applications. *Diamond Relat. Mater.*, 2005, **14**, 1805–1809.