# OBTAINING OF ULTRAFINE POWDER COMPOSITES OF TUNGSTEN, MOLYBDENIUM, TITANIUM AND BORON CARBIDES USING LIQUID PRECURSORS

**Natia Barbakadze [1], Ketevan Sarajishvili [1], Roin Chedia [1], Levan Chkhartishvili [2, 3, *], Otar Tsagareishvili [2], Archil Mikeladze [2], Margalita Darchiashvili [2], Vakhtang Ugrekhelidze [4]**

*[1] Petre Melikishvili Institute of Physical & Organic Chemistry, Ivane Javakhishvili Tbilisi State University, 31 Anna Politkovskaya Street, Tbilisi, 0186, Georgia*

*[2] Boron-Containing & Powdered Materials Laboratory, Ferdinand Tavadze Metallurgy & Materials Science Institute, 10 Elizbar Mindeli Street, Tbilisi, 0186, Georgia*

*[3] Engineering Physics Department, Georgian Technical University, 77 Merab Kostava Avenue, Tbilisi, 0175, Georgia*

*[4] Quality Management Department, National High Technology Center of Georgia, 21 Petre Kavtaradze Street, Tbilisi, 0186, Georgia*

** chkharti2003@yahoo.com*

True solutions and suspensions are widely used for obtaining the nano-sized ceramic composite powders. Selection of appropriate solvent depends on the nature of the initial substances. Usually, choosing of one solvent both for molecular and ionic compounds is impossible, since the solvent must simultaneously be an active carbon source. Previously, we have developed methods for preparing liquid and melt precursors, based on which ultrafine metal carbides and two-phase composite (WC, $Mo_2C$, TiC, $B_4C$, TiC–Ni, $B_4C$–$TiB_2$, WC–Co, $Mo_2C$–Ni, etc.) powders were obtained [1].

As for the technology developed here, it includes following steps:

1. (a) Preparation of true solutions by diluting / reacting the appropriate compounds and organic solvents; and (b) Obtaining of homogenized suspensions of insoluble compounds.
2. CVD (chemical-vapor-deposition) process of volatile compounds or their pyrolysis in preheated (at temperatures > 400 °C) furnace.
3. Grinding of precious precursors and subsequent thermal treatment (carbonation or boration) at temperatures > 1250 °C.

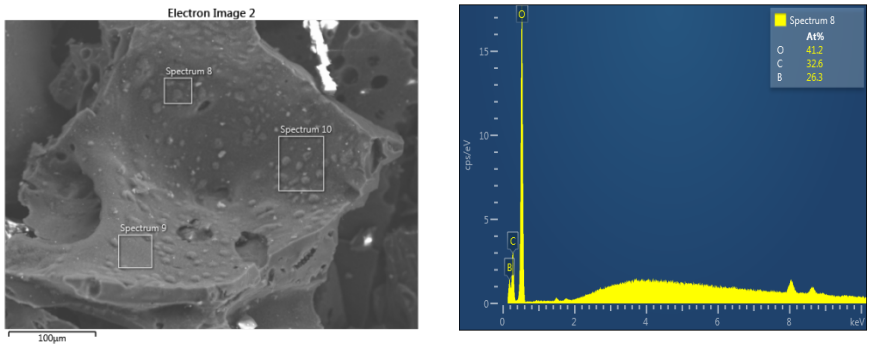
Solutions, as well as melts and suspensions, can be used for receiving of carbides or matrix ceramic composites. For example, by melting ammonium tungstate, ammonium molybdate, nickel chloride, cobalt chloride, and hexamethylene tetramine at 140 – 160 °C and further pyrolysis the WC, $Mo_2C$, WC–Co, and $Mo_2C$–Ni powders are obtained.

Presents work includes study of possibility to obtain boron carbides ($B_4C$) and $B_4C$-composites from various liquid precursors from boron and carbon compounds. In particular, boric acid esters (borates) with alcohol radicals of different structures (ROH, $R'(OH)_2$, $R'''(OH)_3$, polyols, oligomers, etc.) have been tested. In case of the use of volatile borates $B(OR)_3$ (R = $CH_3$, $C_2H_5$, and $C_3H_7$) the CVD process (at > 500 °C) was used in order to obtain boron carbide precursors.

Utilizing previously developed by us technology [2], the treatment of the viscous products obtained by interaction of boric acid with polyols and polymers was carried out by pyrolysis of liquids at 400 – 800 °C in preheated furnace in air. It is confirmed that viscous liquids can be diluted with water. The advantage of this technology is to get two- and multi-component ceramic composite powders in one stage, and in the powder the components are homogenized and are uniformly distributed throughout the powder. The same method is successfully used when small amounts of dopants are inserted. Our results are in full agreement with later reports [3, 4].

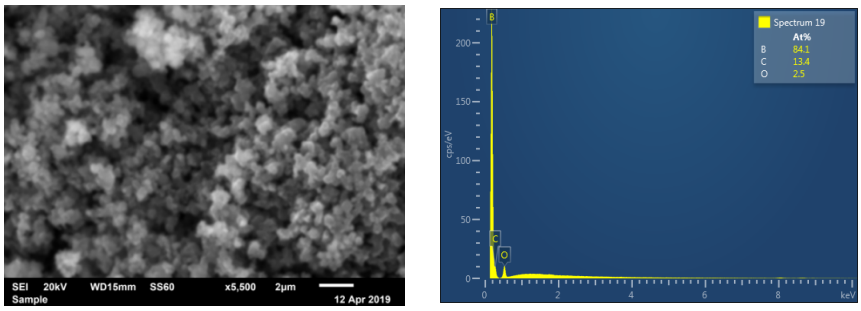
The composite with the same composition was received from various systems, e.g. $B_4C$–20%$TiB_2$ was obtained from $B(OR')_3$+$Ti(OR'')_4$ solution; and the same ceramic composite was obtained from suspension containing $H_3BO_3$–$TiO_2$–glycerine system (Fig. 1). It is established that particles size of $B_4C$–$TiB_2$ composite powder is within the range of 50 – 70 nm [5, 6].

In the well-known methods, this composition is made by mixing or sintering of finished powders. That is why their dispersion does not achieve the nano sizes. During the pyrolysis of organic components different quantities of active carbon are obtained. When using oxide components, carbon oxidation in air flow under controlled conditions (at 700 °C) was used to remove excess carbon from precursors or also well known methods used to produce active carbon (800 – 900 °C).




**(a)** **(b)**

Fig.1. SEM image **(a)** and EDX spectrum **(b)** of $H_3BO_3$–glycerine precursors, pyrolyzed at 800 °C in air.




**(a)** **(b)**

Fig.2. SEM image **(a)** and EDX spectrum **(b)** of amorphous boron–glycerin precursors pyrolyzed at 500 °C under argon atmosphere.

Pyrolysis of homogenized suspensions obtained on the basis of amorphous boron is carried out at 350 °C in air or in the inert atmosphere at temperatures up to 800 °C (**Figure 2**). The optimum content of carbon is determined experimentally and in pyrolyzed precursor it reaches 18 – 25 %. After the grinding of the resulting product, its thermal treatment is performed under an inert atmosphere at temperatures up to 1250 °C. It is confirmed that adding of titanium and zirconium compounds ($TiO_2$, $ZrO_2$, $TiH_2$, $ZrH_2$, etc.) to the precursors promotes low-temperature synthesis of boron carbide.

## Acknowledgement

This work was supported by 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.

## References

[1] ISTC Project # G–462: *New Hard Alloys with Nanocrystalline Components* (2001–2003).
[2] STCU Project # 4600: *Tungsten, Titanium, and Boron Carbide-Based Nanocrystalline Hardmetals* (2009–2011).
[3] Shawgi N., Li S.X., Wang S., Li Y. & Ramzi R. *Ceram. Int.* **44** (2018) 9887-9892.
[4] Watts J. *Controlled Synthesis of Boron Carbide Using Solution-Based Techniques*, PhD Thesis. Brisbane: Queensland Univ. Technol. (2018).
[5] Tsagareishvili O., Mikeladze A., Chedia R. & Chkhartishvili L. Method of obtaining boron carbide based hard nanocomposite materials. *National Center for Intellectual Property of Georgia "Geo Patent"* – Patent # GE P2018 6709 B, 2018 October 11.
[6] 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.: Struc. Funct. & Bioceram.* (2019) – *in press*.