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UNTRADITIONAL SYNTHESIS OF BORON-CONTAINING SUPERHARD AND REFRACTORY MATERIALS - A REVIEW

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Abstract

Boron-containing ceramics find large application in production of superhard and high-temperature materials with application in nuclear and aerospace techniques, military industry etc. The synthesis methods are decisive for the complexity of chemical, morphological and technological properties of these materials. The traditional high-temperature synthesis methods have some disadvantages leading to inconstancy of the product composition due to the boron evaporation, degradation of the furnace materials and contamination of the products, high energy losses etc. Here we show the advantages of some untraditional synthesis methods like direct mechanical synthesis and self propagating high-temperature synthesis (SHS) in the production of titanium diboride (TiB_2), zirconium diboride (ZrB_2) and production of dense boron carbide (B_4C) based materials. Using SEM, TEM, XRD and analytical chemical methods, it was shown that diborides of titanium and zirconium have appropriate properties for production of dense ceramic materials. Using the method of mechanically-assisted sintering high-dense B_4C-based ceramic materials was obtained. It was shown that the mechanical properties of materials obtained by pressureless sintering are close or overcome the corresponding properties of boron carbide densified by the method of hot pressing. The possibility to produce B_4C-based ceramics with controlled properties was also shown.

Keywords: Titanium Diboride (TiB_2); Zirconium Diboride (ZrB_2); Boron Carbide (B_4C); Mechanical Assisted Synthesis; Activated Pressureless Sintering.

Introduction

Boron compounds with the transition elements from IV-VI group and with some non-metals such as C and N possess combination of attractive properties which determine the interest in the fields of synthesis and sintering of these materials. The diborides of titanium (TiB_2) and zirconium (ZrB_2) are typical representatives of the metal-like boron compounds. They have high melting points (3200˚C and 3250˚C) and high hardness values (30.0 GPa and 36.0 GPa), respectively. These materials also have a high resistance to oxidation at elevated temperatures and are stable in metal melts (Al, Cu, Mg, Zn, Cd, Fe, Pb) and slags Schwetz et al., (1981); Graham *et al*., (1971) and Sigl, (1990). Evaporators, crucibles, nozzles, cutting tools and electrodes in the aluminum industry are among the articles produced from the titanium and zirconium diborides using the methods of the powder metallurgy by Graf von Matuschka, (1974); Greenwood and Thomas, (1973). The preparation methods of titanium diboride and zirconium diboride powders are decisive for the chemical, physical and technological properties of the products. Transition metal borides are usually produced by the reduction of the corresponding metal oxides and boron oxide with carbon at high temperatures. These methods proceed in graphite high-temperature furnaces at temperatures overcoming 1600 ^oC. Evaporation of boron and difficulties with obtaining stoichiometric borides, high consumption of energy and graphite, low productivity and high price of the products are among the disadvantages of these methods. The traditional high-temperature synthesis methods of titanium and zirconium borides are described elsewhere Radev and Marinov, (2004) and Guo *et al*., (2012).

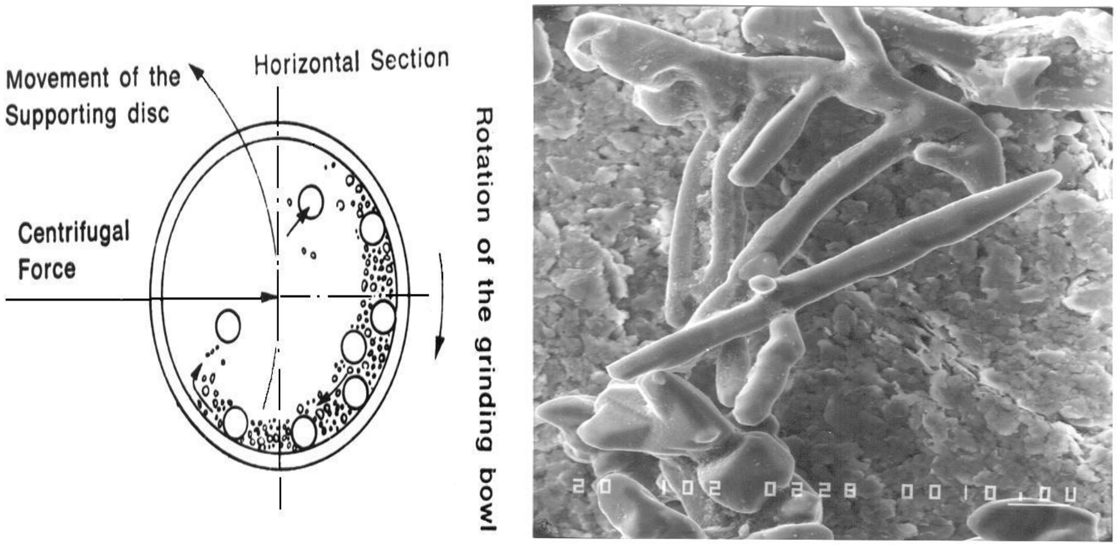
Boron carbide (B_4C) is important high-tech material thanks mainly to its properties and their unique combination. B_4C is the third hardest material (45 GPa) after diamond and cubic BN being incomparable cheaper. It has high value of modulus of elasticity (450 GPa) and high abrasive wear resistance, high melting point (2450^oC), good chemical stability, low density (2.52 $g.cm^{-3}$). These properties determines application of boron carbide dense ceramics in military industry as protective clothing for pilots and ground troops, plates for tanks and helicopters protection, etc. Other industrial uses of B_4C are as abrasive media for lapping and grinding, polishing media for hard materials and as wear resistant components. Another remarkable property of B_4C is the high effective cross section (600 barns) towards thermal neutrons which determines application of dense boron carbide pellets in the design of the control rods systems of different type nuclear reactors. Due to the presence of strong, directed covalent bonds in the crystal lattice, low values of self-diffusion coefficients of B and C, bad plasticity of B_4C and high resistance to grain boundary sliding, the method of hot pressing (HP) is the only industrial way to obtain near theoretically dense B_4C articles. Simple shapes of dense B_4C are industrially prepared by HP under vacuum or inert atmosphere at 2100-2200 ^oC and pressure of 30-40 MPa. This method possesses some disadvantages that reflect on the price of the end product. The method of HP is low-productive, high-energy consuming and uses expensive high quality graphite for press instrument. The products have simple shape and very often additional machining with diamond tools is necessary.

In this paper, we demonstrate the advantages of mechanochemical synthesis of TiB_2 and the self-propagating high-temperature synthesis (SHS) of ZrB_2. The method of activated pressureless sintering of dense superhard B_4C-based materials is also shown.

Materials and Methods

Mechanochemical Synthesis of TiB_2

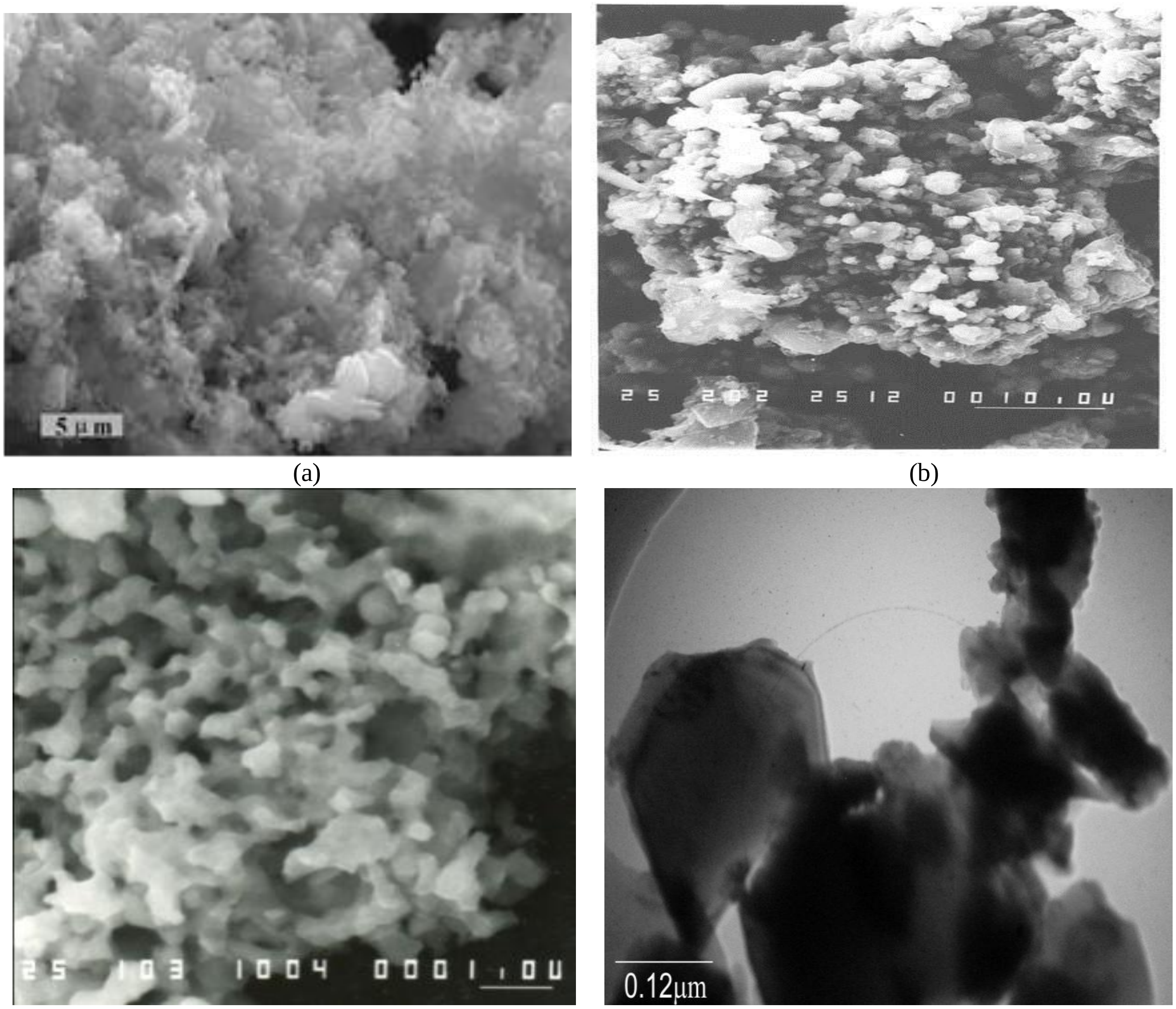
Following the steady establishment of physical metallurgy in the first half of 20th century and then materials science, the potential of mechanically activated processes for materials synthesis was first demonstrated by Benjamin, who devised “mechanically alloying” for oxide-dispersed nickel- and iron-based super alloys Benjamin and Volin, (1974); Benjamin, (1976). This marked a new era of successfully employing mechanically activated process in materials synthesis, and it was followed by the extension and application of this novel technique to a wide range of structural and functional materials, including intermetallics and metal matrix composites, magnetic materials, semiconductors, and more recently nanocrystalline ceramic materials. There exists variety of techniques based on the intense milling of reagents in high-energy apparatuses like planetary type mills and attritors, par example mechanical alloying, mechanical milling, mechanical disordering, mechanically assisted thermal or self-propagating synthesis, etc. Here we demonstrate the direct synthesis of TiB_2 by intense mechanical treatment of Ti and B particles in a planetary ball mill. Fig.1a. shows schematic representation of planetary ball mill in which the high efficiency of the mechanical impacts is due to the antiparallel vectors of movement of supporting disk and milling containers, a complicated trajectory of milling bodies and resulting high accelerations.



(a) (b)

Fig.1 Schematic representation of planetary ball mill (a) and SEM micrograph of Ti Particles (X1000) before milling (b).

A stainless steel bowls and milling balls with diameter 10 mm were used. A stoichiometric amounts Ti and B powders to produce TiB_2 were used as reagents. The SEM image of the initial Ti particles is show in Fig. 1(b). The picture reveals lengthened in shape particles with mean size of 250 μm. The SEM image of amorphous boron particles with mean size of 1-5 μm, used as reagents for the mechanical synthesis of TiB_2 and for the SHS of ZrB_2 is shown in Fig. 2a. After 80 min intense mechanical treatment the synthesis of TiB_2 proceeds by explosive mechanism. Fig. 2b shows SEM image of the product consisting of aggregated particles with uniform size distribution and submicrometric mean sizes. TEM image reveals separated particles with sizes of 150-200 nm (Fig. 2d). XRD analysis of the product reveals presence of phase of TiB_2; the chemical analysis shows presence of almost 29 wt% combined boron and lack of free Ti, B or B_2O_3 Radev, (1996); Radev and Klissurski, (2001). The morphological change of Ti particles in the process of mechanochemical synthesis of TiB_2 is studied in Radev and Klissurski, (2001). The appearance of new active surfaces, increased contact between particles of reagents, presence of local heats and areas of increased pressure are reasons for initiation combustion synthesis. Due to the high enthalpy of the TiB_2 formation, after the period of mechanical activation the process of self-propagating combustion synthesis takes place. Milling-induced combustion was first observed by Tschakarov during the mechanochemical synthesis of metal chalcogenides from a mixture of elemental powders Tschakarov et al., (1982). Subsequently, a number of similar reactions were reported to occur during chemical reduction of oxides with reactive metals under mechanical alloying conditions. The technological advantages of the mechanochemical synthesis are obvious. High-temperature processes and equipments, processes of homogenization and grinding of powders typical of the classical high-temperature syntheses are avoided. The product obtained is finely dispersed which is a precondition for high sinterability of TiB_2 powder.



(a) (b)

(c) (d)

Fig. 2 (a-c) shows the SEM Micrographs of Boron (X 4000) and Zirconium (X 10000) and Titanium Diboride (X 2000) and (d), TEM micrograph of TiB_2 (X86000) particles used in the synthesis.

Despite the technological attractiveness of direct mechanochemical synthesis, the strict safety measures should be taken during experiments with compounds with high enthalpy of formation like borides of the transition metals. The synthesis reactions proceed with strong explosions and opening of the reactors full of milling balls before the synthesis may cause explosion initiated by the penetration of fresh air. The usage of expensive pure elements as reagents is another disadvantage of the method. The synthesis methods based on the mechanical activation of reagents and known as mechanically assisted processes overcome the above mentioned obstacles as reported by Radev et al., (2005).

Self-Propagating High-Temperature Synthesis (SHS) of ZrB2

The self-propagating high-temperature synthesis (SHS) process takes advantage of the energy developed by highly exothermic reactions to synthesize ceramic powders, hence, reducing the production costs associated with the manufacture of some ceramics such as borides or carbides Radev and Klissurski, (2001). Besides the economic benefits, combustion synthesis is a relatively simple and non contaminant method for producing powders of high purity. Nevertheless, it is still of interest to critically study the characteristics of a material processed from SHS powders, compared with a material processed in the same way from typical commercially available powders. An electron micrograph of the initial Zr particles is shown in Fig. 2(c). The particles have an isometric shape and fine sizes, the mean particle size being 1-5 µm. The stoichiometric mixture of Zr and B particles is blended and shaped by cold pressing to form cylindrical pellets.

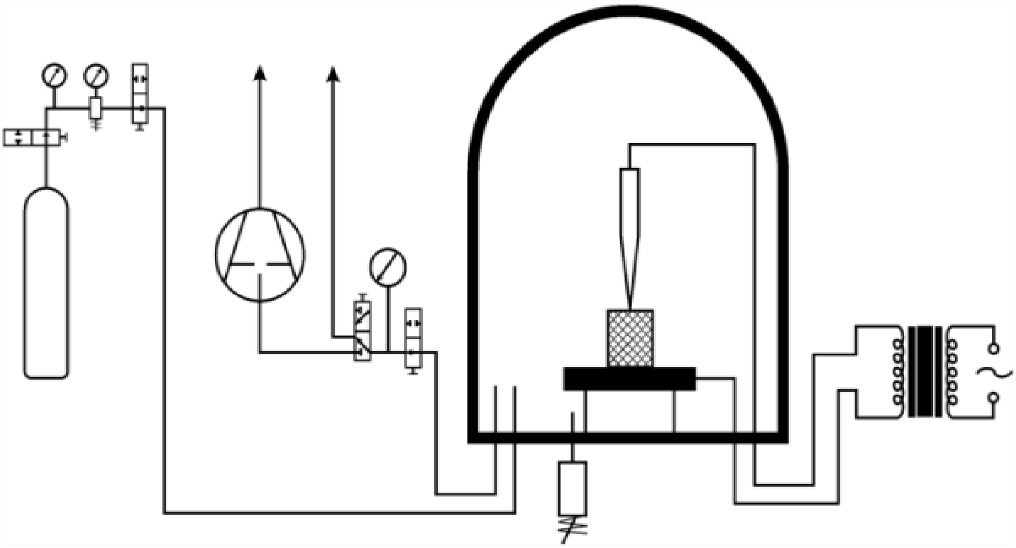


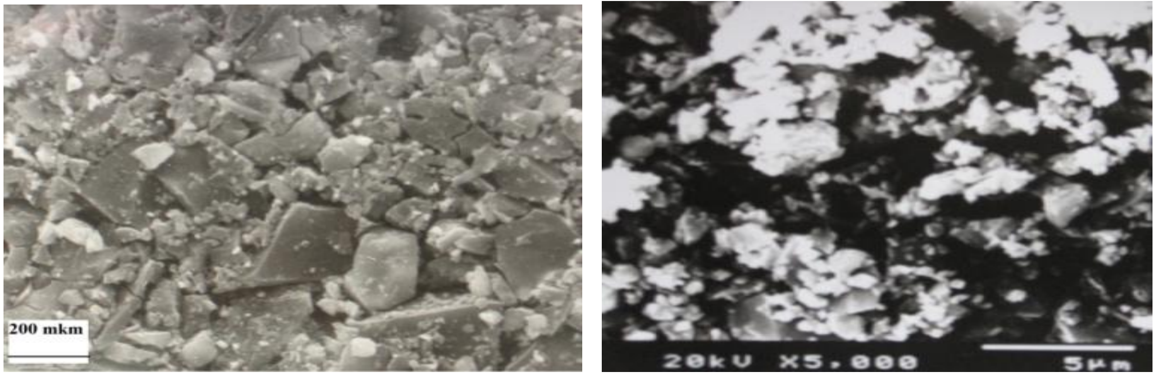
Fig.3. Reactor for SHS of metal borides

The pellets containing reagents have been placed between the electrodes of the reactor as the Fig. 3 shows. The SHS reaction has been started by a single current pulse and the synthesis proceeds with a peculiar hissing sound. The adiabatic temperature during SHS of ZrB_2 and the melting point of the product are similar and for the system like Zr-B, Ti-B etc, the synthesis under conventional combustion conditions are possible. The reaction proceeds in less time than necessary to remove the products from the reactor, which is a good demonstration of one of the advantages of the SHS. The XRD analysis reveals presence of well-crystallized phase of ZrB2 and some traces of ZrO_2. The amount of combined boron in the product is 18.8 wt.% which is close to the stoichiometric amount of 19.2 wt. %. The boron content in the product could be enhanced by adding additional amount of 1-2wt.% B excess to the reagents. Part of the boron evaporates during the SHS due to the high adiabatic temperatures during syntheses of transition metal borides. It is possible to reduce the temperature of SHS by introducing some amounts B_2O_3 or transition metal boride into reagents. The presence of traces of ZrO_2 in the product is due to the high chemical activity of the initial Zr particles and their surface oxidation. Some comparison between properties of TiB_2 and ZrB_2 obtained by SHS using different in their morphological properties starting Ti and Zr particles is shown in Radev and Marinov, (1996). The SEM picture of the ZrB_2 particles obtained by SHS is shown in Fig. 8. The mean size of particles is 10-15 μm and they show the tendency to form aggregates. The presence of many edges with small curvature radii is a premise for the high abrasive ability of the product.

The synthesis methods of refractory metal borides determine the different properties of the products. TiB_2 obtained by mechanochemical synthesis strongly differs in morphological properties from the product obtained by SHS. The role of factors like particle sizes of reagents, contact between particles and pressure efforts of reagents during SHS are discussed in Radev and Klissurski, (2001).

Activated Pressureless Sintering (APS) of B_4C-based materials

Fig.4a shows SEM image of starting B_4C powder before milling in a planetary mill. The particles have non-uniform size distribution and the mean size of about 200 μm. The morphological properties of the particles and the low sinterability of the B_4C determine the necessity of intense mechanical treatment of the initial B_4C powder before sintering. Fig. 3b shows the SEM image of the same powder after 4 hours milling in a planetary ball mill.



(a) (b)

Fig.4a-b present the SEM of B_4C before milling at X300 and after 4 hours of milling at X5000 respectively

As a result of the intense mechanical treatment, the particles of B_4C become smaller and the milling leads to accumulation of different types of defects in the crystal lattice. Previous XRD investigations have shown that as a result of the intense milling, nanocrystalline boron carbide particles with a mean size of 88 nm are obtained Radev, (2010). Well-developed surface area of the milled B_4C particles and their nanocrystalline structure are preconditions for their higher sinterability, Uskokovic and Exner, (1990).The reason for the low sinterability of B_4C is the presence of strong prevailing covalent bonds in its crystal lattice. Breaking these bonds during the sintering by appropriate chemical interaction between B_4C and the sintering additive could be the reason for enhanced diffusion mobility of the atoms involved into interaction and the better sinterability of the material. To activate the densification of B_4C we use high-temperature solid state replacement reactions which could be demonstrated by Reaction.1:

$$\mathbf{B_4C + Me^{IV\text{-}VI}C \rightarrow Me^{IV\text{-}VI}B + C} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{(1)}$$

Transition metal carbides from IV-VI group marked as $Me^{IV-VI}C$ and used as additives during pressureless sintering of boron carbide have a number of advantages as compared to the corresponding metal oxides or other additives used for the same purpose. According to the model of Aselage and Emin, carbon saturated composition near to B_4C ($B_{12}C_3$) consists of $B_{11}C_2$ icosahedra and C-B-C chains Aselage and Emin, (1991)**.** Reducing the carbon content in boron carbide and moving the composition from B_4C to $B_{6.5}C$ ($B_{13}C_2$) leads to chain transformation from C-B-C to C-B-B. The last ones are less rigid in comparison with C-B-C chains and are the reason for lower values of dynamic mechanical characteristics such as shear modules, critical amplitudes of oscillatory deformation and shear elastic of $B_{6.5}C$ by Lezhava *et al*, (2006). Using $Me^{IV-VI}C$ as additive is a way to preserve the carbon content in the B_4C lattice. The high-temperature chemical interaction of oxygen-free additives with some amount of B_4C does not lead to evolving CO or other gases which is inadmissible during the process of sintering. The role of carbon in the process of densification of B_4C is also very important. Carbon or carbon-containing precursors have been largely used as sintering aids in amounts of 3-5-wt.% Schwetz and Vogt, (1998): Schwetz and Greller, (1981) and Suzuki, Hase, Maruyama, (1979). When transition metal carbides are used as sintering additives, the active carbon is formed in situ as a result of the high-temperature interaction. Fig. 5 shows an optical micrograph of B_4C sintered in the presence of 10 wt. % WC at 2250°C. As a result of the high-temperature interaction according to React.1 and the process of sintering, a dense B_4C-W_2B_5 material with relative density of 97.1% is obtained. The structure is almost pore-free as a result of activated pressureless sintering process.

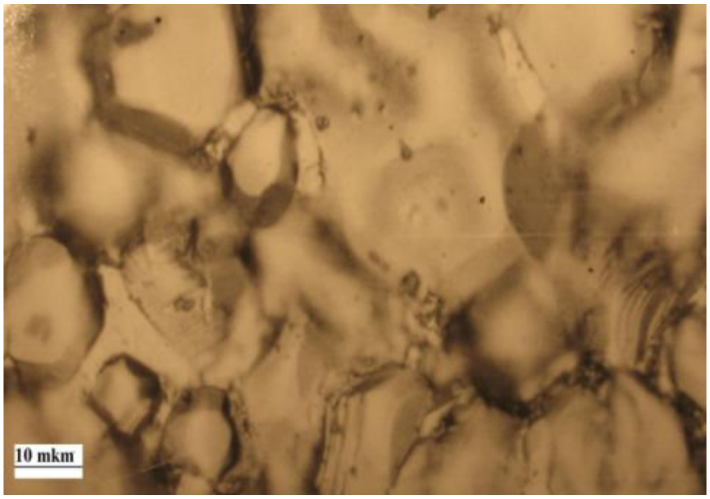
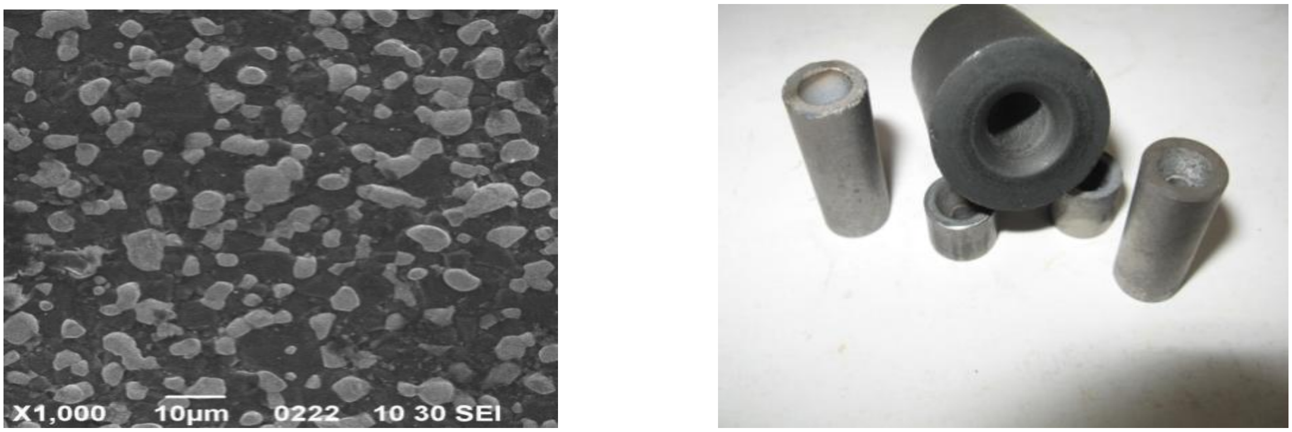


Fig.5. Optical micrograph: B_4C-10 %W_2B_5, X1000

The mean size of the B_4C particles is about 10 μm, which is a precondition for high mechanical properties. Among the boron carbide grains there are secondary obtained B_4C-W_2B_5 grains. The structure is typical of materials sintered in the presence of eutectic liquids. The possibility to obtain a variety of boron carbide-based materials changing the sintering aids is based on the existence of high-temperature eutectic melts in the systems B-C-Me^{IV-VI} Schouler, Ducarroir and Bernard (1983). It was shown that the microhardness values and the abrasive wear resistance of B_4C-W_2B_5 and B_4C-CrB_2 surpassed the corresponding properties of hot pressed B_4C according to Radev *et al*. (1998). The possibility to create new B_4C-based materials using the cheaper method of the pressureless sintering is demonstrated by the in situ synthesis of a B4C~10%HfB_2 composite material. Fig. 6(a) shows the dense structure with relative density of 95.9% and random distribution of particles HfB_2-lighter in color. Hafnium boride is attractive as neutron-absorption material due to its appropriate thermophysical properties and high neutron absorption ability on B and Hf atoms. The technological advantages of the method of pressureless sintering of B_4C using some transition metal carbides as sintering aids and the high mechanical properties of the materials obtained are a good basis for the producing of large scale particles with industrial application. Fig. 6(b) shows sand-blasting nozzles with composition B_4C-10 wt.% W_2B_5 produced by the method of activated sintering. They have application in dentistry and metallurgy and overcome in life service their hot-pressed boron carbide counterparts. The advantage of the described method is the possibility using the method of pressureless sintering to obtain a large scale B_4C-based materials which properties could be arrange in advance.



(a) (b)

Fig. 6a-b show the SEM of B_4C-10 % HfB_2 using PS and Sand Blasting nozzles using APS

Conclusion

The advantages of MAS and SHS in the production of TiB_2 and ZrB_2 have been shown. These modern methods improve the yield, purity and make the application of super-hard refractories in industry versatile compared to hot pressing. Highly dense B_4C was also produced using APS.

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