Investigation structure and properties of heterogeneous materials based on submicron powders of boron carbide, produced by hot-pressing

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Abstract. This paper discussed the microstructure and mechanical properties of ceramic tablets obtained from mixtures of boron carbide-based powders with various submicron additives. As the main powder for the study was used crystalline powder of boron carbide brand F400 (PJSC "Zaporizhia Abrasive Plant") with an average size of 20 microns. Submicron powders of boron carbide, boron nitride and carbon nanotubes were used as additives. It is shown that with the hot pressing parameters used, active sintering does not occur. Sintered tablets based on boron carbide F400 with additions of 10% by weight have the same hardness as tablets obtained from submicron powders. These additives could be perspective for further applications.

1. Introduction

For ceramic powders with a high melting point, the use of cold pressing is practically not feasible due to the extremely low rate of diffusion flowing in the substance. The process of hot pressing allows producing sintered compacts from the powder. Mechanical properties of these compacts can be described by the behavior of a continuous heterogeneous deformable solid. With a decrease in the dispersion of the powder, diffusion processes are significantly accelerated, which leads to an increase in both the sintering rate and the strength of the sintered material [1, 2]. At the same time, reducing the dispersion makes it difficult to predict the form and size of the resulting product, since the amount of shrinkage becomes significant. Production of dense products from boron carbide-based materials with high values of hardness and strength is possible when sintering temperature is about 0.9 of melting temperature and pressure reached above 60 MPa. These technical requirements significantly limit the product range and the volume of production of superhard ceramics. Researchers are trying to decrease the temperature and sintering pressure by applying novel methods of compaction, mechanical activation, alloying additives [3-5]. The purpose of this work is to obtain the dependence of the hardness of hot-pressed tablets based on boron carbide on the composition of the alloying additives. Selection of the additive and the method of consolidation are generally dictated by the end use of the product and the properties that are required. The additive by itself or due to in situ reaction with boron carbide would form a non-volatile second phase aiding in densification and property enhancement.
2. Materials
As the base powder for this study were used crystalline powder of boron carbide brand F400 and F1200 (PJSC "Zaporizhia Abrasive Plant") with an average size of 20 and 3 microns respectively. Submicron powders of boron carbide, boron nitride and carbon nanotubes were used as additives (table 1). Obtaining submicron powders of boron carbide was carried out by reducing boric acid with carbon. Carbon nanotubes (CNT) participated in the interaction with boric acid, and boron oxides are remnants of unreacted boric acid. Grinding and mixing of the powders after preparation of the mixtures was carried out in a ball mill for one hour. Mixing with additives of boron nitride was carried out after the synthesis of boron carbide by weight.

3. Methods
For uniaxial hot pressing of tablets, a compact automatic laboratory hot press was used. This is periodic action set-up with indirect resistance heating, bottom loading elevator-type and autonomous water cooling system of closed type. The internal camera in the hot zone filled an inert gas (argon). Heater and insulation made of carbon materials and the possibility of manual and automated controls. As the mold was used to press has the cylindrical form with outer and an inner diameter of 40 mm and 16 mm respectively. As a result, samples were obtained in the form of tablets (cylinders) diameter 15.8-16.0 mm and a height of 2 to 3 mm. The walls were built of matrix graphite paper to extend the life of the graphite mold. The sintering parameters were chosen as low as possible to produce solid tablets. Heating of powder mixtures in a graphite mold was carried out at a rate of 50 °C/min in argon atmosphere. A powder weighing 2 g was poured into a graphite matrix with a diameter of 16 mm. The maximum heating temperature was 1700°C, the pressure was −25 MPa. Hot-pressing at maximum parameters was carried out during 15 min. These parameters are reliable to early stage of sintering (solid phase sintering) of the powder when solid particles of boron carbide powder are sintered at the points of contact between the particles. Low rates of powder sintering are necessary to control the potential exothermic reactions of additives with the powder and the material of the mold, as well as to extend the service life of the mold. Low rates of powder sintering are necessary to control the potential exothermic reactions of additives with the powder and the material of the mold, ensure durability of the mold. The resulting tablets are easily removed from the graphite mold, able to retain their shape.

4. Microstructure
The cross-section of produced tablets was polished for further analysis using a Zeiss EVO MA 15 scanning electron microscope (SEM) and an Oxford Instruments INCA X-Max energy dispersive analyzer (EDX) (Table 2). It is shown there are many pores and cracks in all tablets. If there are impurities in the tablet, the pores move to the impurities; for materials without impurities (F400 and F1200), the pores begin to dissolve in the tablet material. The sizes of cracks and pores for samples with additives are approximately the same and range from 1 to 20 microns. Grains of boron carbide do not completely sinter and there are iron additives between grains (figure 2a, c, d, and e). EDX-analysis evidenced presence of iron in all tablets and nitrides in tablets with boron nitrides (table 2). Besides in samples with boron nitride high oxygen concentration detected. This is due to the additives are obtained.
by reducing oxygen from boron oxides and nitrogen. Mixing various boron carbide powders and mechanical activation in a ball mill leads to an elevated iron content in sintered tablets of up to 3 percent by weight. Other impurities were less than 0.5% wt.

Table 2. EDX-analysis of hot-pressed tablets.

| Mixture name | F400 | F400MA | F400+10%B2O5,B4C,BOC | F400+10%BN | F400+10%BN+1%CNT | F1200 |
|--------------|------|--------|-----------------------|------------|--------------------|-------|
| Elements     |      |        |                       |            |                    |       |
| B            | 73,95| 68,22  | 67,82                 | 70,75      | 73,77              | 77,62 |
| C            | 22,97| 29,12  | 26,44                 | 18,12      | 18,81              | 20,73 |
| O            | 0,82 | 0,63   | 2,73                  | 3,52       | 2,28               | 0,74  |
| Fe           | 0,06 | 1,69   | 2,51                  | 3,05       | 1,98               | 0,10  |
| Al           | 0,11 | 0,15   | 0,11                  | 0,21       | 0,10               | 0,05  |
| Ca           | 0,30 | 0,14   | 0,26                  | 0,26       | 0,30               | –     |
| Cr           | 0,07 | –      | 0,13                  | 0,14       | 0,09               | –     |
| Si           | 0,09 | 0,05   | 0,27                  | 0,32       | 0,26               | 0,76  |
| N            | –    | –      | 3,62                  | 2,40       | –                  | –     |

Figure 1. SEM-images of cross-sections hot-pressed tablets with magnification X4000:
- a - F-400;
- b - F-400+MA;
- c - F400+B2O5; d - F400+BN;
- e - F400+BN+CNT; f - F1200.

5. Microhardness

The study of microhardness was carried out on a Wilson Hardness Group Tukon1102 microhardness tester with a load of 1 kg (figure 2). The last column is the hardness of boron carbide sintered at pressure 90 MPa and temperature 2350 °C. Powders F400 and F400+MA crashed under indenter loading. Boron carbide grains split off from sample therefore hardness values could not be set correctly. Other tablets demonstrate similar hardness values slightly smaller as compared to fine powder (F1200). Submicron additives could work as sintering process accelerators at the given hot-pressing parameters. The rise of microhardness is attributed to the presence of oxide layer which helps in precipitation of B4C through liquid B2O3. These data are confirmed by other researchers [5].
The obtained tablets exhibit loose structure, high porosity and a large amount of iron in the samples, which is directly related to insufficient parameters of temperature and pressure. The hardness of the obtained tablets corresponds to the hardness of boron carbide with small impurities (up to 4% by weight) of pure boron or carbon [5]. Nevertheless, the mechanical activation and the addition of carbon in the form of nanotubes ensure the activation of sintering processes, and could be perspective in feather applications such as selective laser sintering [6].

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