Boron carbide morphology changing under purification

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Abstract. Boron carbide synthesized by using coaxial magnetoplasma accelerator with graphite electrodes was purified by two different ways. XRD-investigations showed content changing and respectively powder purification. Moreover TEM-investigations demonstrated morphology changing of product under purification that was discussed in the work.

1. Introduction

Boron carbide attracts a great interest because of low weight, high hardness, high chemical and temperature resistance and neutron absorption capability [1]. According to that it finds a lot of applications in different areas such as wear resistant materials, cutting tools, reinforcing of metal and ceramic composites and neutron absorbers of control rods for nuclear reactors [2]. Thus a lot attempts has been done to find the most effective method of synthesis for producing nanosized boron carbide. The most spread of them are carbothermal reduction [3], zol-gel method [4], mechanochemical synthesis [5], SHS process [6] and gas-phase synthesis [7]. Another attempt to synthesize nanosized boron carbide was done in [8] by using coaxial magnetoplasma accelerator with graphite electrodes [9-12]. Obtained product consists of crystalline boron carbide with a small amount of impurities such as graphite and boron oxide. In the present study different efforts to purify synthesized powder were done and as a result on of them lead to morphology changing without any crystal structure modification.

2. Experimental

Purification of obtained powder was done in two ways. In the first case powder was only washed by hot water to remove boron oxide and in the second case powder firstly was annealed at 600 0C for an 60 minutes to oxidize graphite and then washed also. Slurry mixture of powder in the water was boiled about 20 minutes then precipitated. After that water was pour off and the remaining residue was heated at 100 0C until full drying using Nabertherm P310 furnace. Initial and purified powders were investigated using XRD (Shimadzu XRD7000S, Cu-Ka) and TEM using Philips CM12 electron microscope.

3. Results and discussion

Figure 1 shows XRD data of synthesized and purified powders. XRD-investigations (figure 1a) show that initial powder consist of crystalline boron carbide [PDF4+, # 01-075-0424] as main phase and boron oxide [PDF4+, # 00-006-0297] and graphite [PDF4+, # 01-075-1621] as impurities in a small amount. XRD-pattern (figure 1b) of purified by washing product shows disappearing of boron oxide which forms boric acid dissolved in water by following reaction:

$$B_2O_3 + 3H_2O = 2H_3BO_3 \quad (1)$$

In comparison with initial product intensity of graphite decreases because of boron oxide washing out from boron carbide surface and respectively decreasing of X-Ray radiation absorption by boron oxide.

XRD-pattern of product after annealing shows the same result but graphite intensity increases. The temperature of annealing was chosen on the border of boron carbide and graphite oxidation to decrease boron carbide losses and maximally oxidize carbon. Powder after annealing was covered by boron oxide glass and after washing in a hot water this boron oxide glass was dissolved and free up powder particles from glass cover. Graphite intensity increasing demonstrate that heat treatment temperature was not enough to oxidize the carbon but boron carbide undergoes oxidation and mass lose with decreasing of intensity on XRD-pattern.

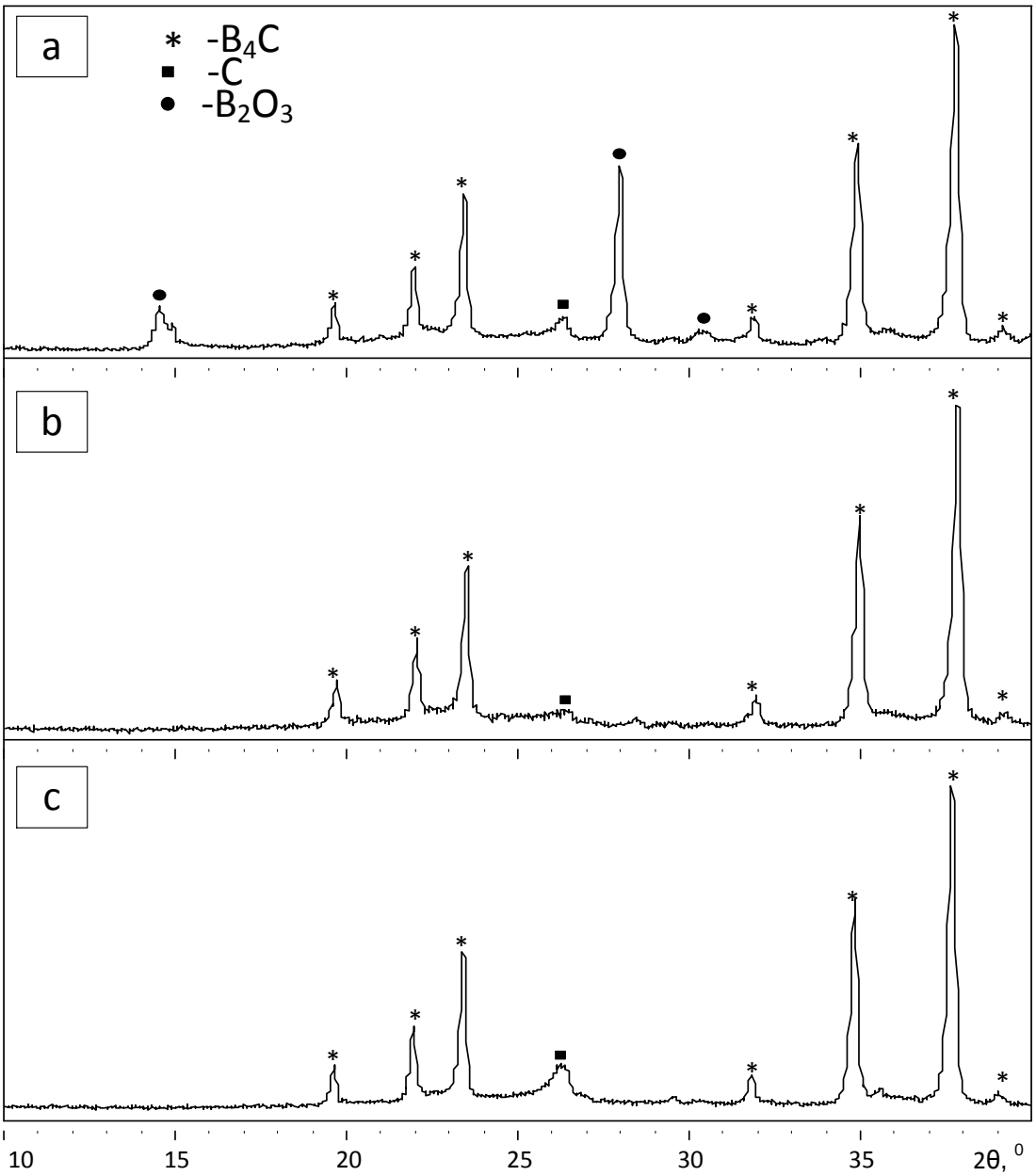

Figure 1. XRD data of initial (a), washed (b) and annealed (c) powder of boron carbide.

TEM-investigations of powder product shows that particles undergoes morphology changing after heat treatment in comparison with initial powder as it can be seen at figure 2. After annealing particles became smaller and loose classical morphology as on figure 3*a* and 3*b*. Therefore because of annealing influence on particles morphology to determine a role of temperature for morphology additional investigations were done. Powder product was annealed in the range of temperatures from 300 up to 580 ^{0}C to exclude boron carbide oxidation and boron oxide vitrification. As it was shown that product does not support structural transformation it was investigated only by TEM presented at figure 3. Particles treated at 300 ^{0}C does not undergoes any morphology transformation and consist of classical particles but when temperature gets to 400 ^{0}C a low amount of rectangular particles appear in the product. Significant morphology changing occurs at 500 ^{0}C with formation of a large number of crystals with right shape and sizes that do not exceed 100 nm. Also a small amount of large crystals (500 nm) with classical shape are persisting in product.

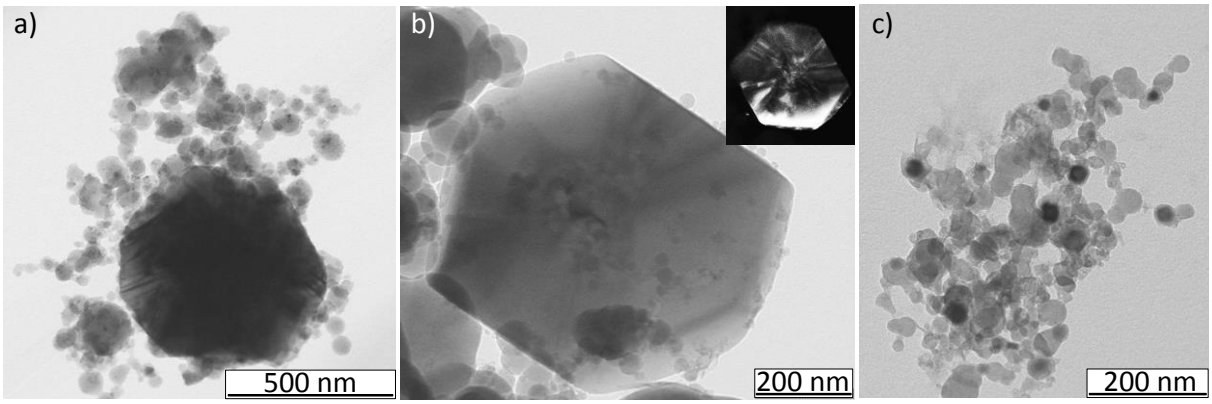

Figure 2. TEM data of initial (a), washed (b) and annealed (c) powder of boron carbide.

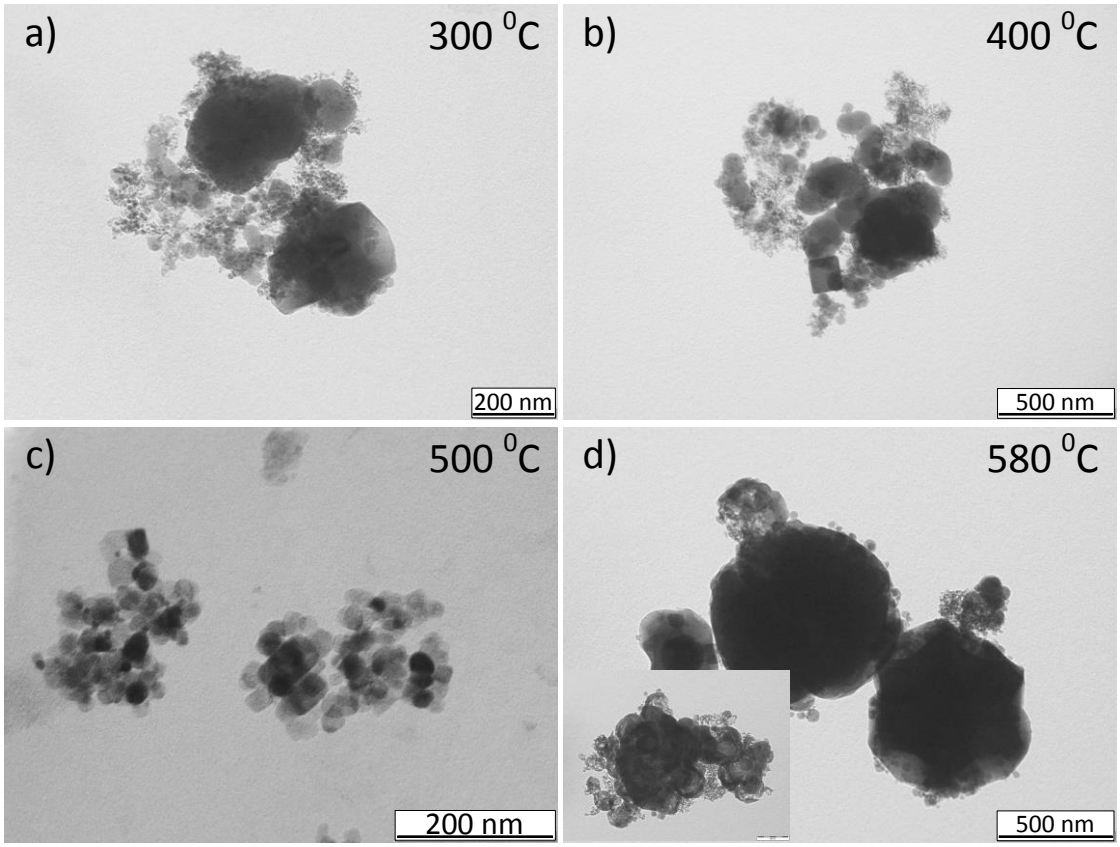

Figure 3. TEM data of annealed powder of boron carbide at different temperatures.

Only large crystals with classical morphology (500 nm) are in product when temperature become 580 ^{0}C. Besides them a new particles are formed at that conditions and have circular shape with thickening on the edges. Also very small fraction is formed with particle sizes less than 40 nm. It is suggested that fine fraction of boron carbide powder oxidize due to the low thermal stability of nanosized particles because of small size.

Conclusion

In accordance with presented data and TEM-capture at figure 4 boron carbide particles might have segmented structure with weak connections in crystal that disintegrate under heat treatment. Moreover synthesis of the same rectangular crystals under lower pressure (P0=0.1 atm.) explained by higher speed of plasma flow because of lower gas resistance. This leads to increasing of crystallization and cooling rates that forms crystals with smaller sizes and different morphology. Increasing of synthesis pressure and decreasing of plasma flow speed respectively leads to increasing of condensation, crystallization and cooling duration. That creates conditions for self-assembling of nanosized rectangular crystals to polyhedral formations with weak connection of them.

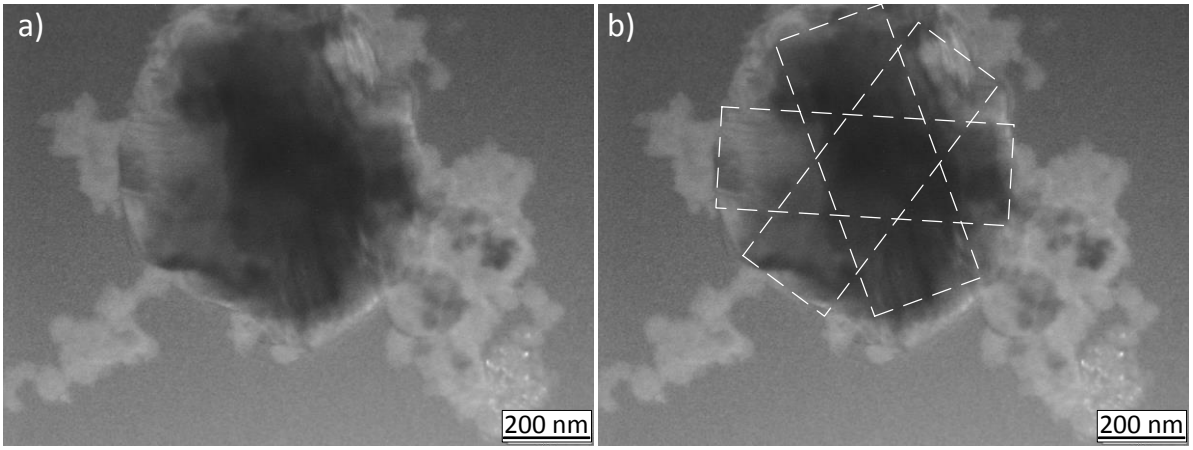

Figure 4. TEM data of boron carbide particle with classical morphology

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