XRD Investigation of SHS-Produced Boron Carbide
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Abstract
Boron carbide with compositions corresponding to the homogeneity region in its phase diagram was obtained by self-propagating high temperature synthesis (SHS). The received samples were characterized by X-ray diffraction (XRD) analysis, lattice parameters and half-width of reflections have been investigated. The lattice parameters of boron carbide reported in the literature exhibit a too wide spread in their values for equal carbon content. It is unusually for covalent compounds such as boron carbide which has strong chemical bonds. The largest spread in lattice parameters was observed at 13.2% (atomic) of carbon in boron carbide. In other hand, for SHS-produced samples the spread was minimal. Using XRD analysis cell parameters of boron carbide in our experiments was found to depend on carbon concentration in non-linear way. Lattice parameter was found to reach the unusually high value of 12.31 Å. The half-widths of boron carbide diffraction lines were found to depend on carbon concentration and reach their maximum values at 13.2 atomic % of carbon when the lattice is most disordered. The structure analysis allows to associate it with the process of crystal structure ordering caused by replacement of boron atoms by carbon ones during formation of boron carbide structure. The carbon atoms can be incorporated into different positions in both the linear groups and the icosahedra. In other words, some certain composition can correspond to different structure. Therefore, both experimental data and crystal-chemical considerations allow to conclude the possibility of different kinds of ordering in boron carbide structure, resulting in instability of lattice parameters and consequently in properties.

Introduction

Due to the unique properties – such as high melting point, hardness, modulus of elasticity chemical and corrosion resistance, neutron-capture cross-section, and low density – boron carbide is exceedingly valuable for practical implementations and used as abrasive and cutting material in industry, as a substance of reactor rods in atomic power engineering, and thermo- and electrical insulating material in microelectronics.

Boron carbide (structural type B₄C) is a phase of variable composition with wide range of homogeneity (8-20 at.%) [1, 2] that corresponds to B₁₁₅C – B₄C. A wide spread in B/C ratio means that structural type remains uncharged and ordering of carbon atoms can take place in a different fashion which sufficiently influences boron carbide properties especially electrical and temperature ones [1].

The crystal structure of boron carbide is described with 2 structural units: icosahedron consisting of 12 atoms and 3-atomic linear group. Such matters as sequence and site of replacement of boron atoms by carbons ones are still the subject of discussion. Another unanswered question is a too wide spread in the values of lattice parameters for the same chemical composition in literature as well as dependence of the parameters on carbon content.

The first data on crystal structure obtained by X-ray diffraction [3, 4] showed that boron carbide has a hexagonal system (space group R 3 m) consisting of icosahedra B₁₂ and linear groups C–C–C [3] or C–B–C [4] in its structure. Later, structural and spectral investigations showed that boron carbide is a phase of variable composition and its properties is a function of carbon content (σ) that can vary between 8 and 20 at.% [1, 2]. Figure 1 presents a wide data spread in values reported by various authors [1-15], the largest inconsistence was for σ ≈ 10-13 at.%.

In this communication, we report on more than 15 different compositions of boron carbide produced by SHS and examined by XRD analysis.
Synthesis of boron carbide was carried out in SHS mode by the following scheme:

\[ 2\text{B}_2\text{O}_3 + 6\text{Mg} + x\text{C} \rightarrow \text{B}_4\text{C}_x + 6\text{MgO}. \]

The SHS mode was chosen due to its simplicity, transiency, and relatively constant conditions for phase formation in all volume of initial mixtures. The final product consisted of particles of the same size (~ 5 μm).

The \( \text{B}_2\text{O}_3/\text{Mg} \) ratio was kept constant. The carbon content of initial mixtures was adjusted so that in a final product \( \sigma \) would have a value from 5 up to 30 at.% (in case of complete incorporation of all carbon into boron carbide). However, the experiments have shown that combustion of the mixtures containing above 20 at.% of carbon yielded the products containing free carbon. Therefore, the nominal carbon contents in boron carbide agreed with the measured ones only for \( \sigma \) below 20 at.%. The composition of final products was controlled by a chemical analysis, it was shown that carbon is kept in the mode of SHS.

After intermixing in a roller mill, bulk-density initial mixtures were placed into a reactor and ignited with a wire under Ar (3 MPa). Charge weight was about 200 g. Synthesis temperature reached a value of around 2000 °C. Resultant cakes were crushed in a jaw breaker and then in a drum mill. Unreacted Mg and MgO were removed by washing with dilute HCl. The particle size of final product was about 5 μm.

XRD investigations were carried out on automatic powder diffractometer with Cu-Kα radiation. The method of internal standard was used; a reference sample (10 wt.% of silicon) was added to the samples researched. Lattice parameters of boron carbide were calculated using “Burevestnik” software; the accuracy of calculations was about of 0.001-0.005 Å.

Results and Discussion

Figure 2 presents typical XRD patterns of boron carbide with different \( \sigma \). A broad halo with maximum at 22.0° is related to a cell of amorphous quartz used as a substrate for the researched samples. It can be seen a general similarity of XRD patterns, reflecting their belonging to the same structural type. However, there are some systematic differences related to the carbon concentration. Peaks of pure boron and magnesium borate are visible on patterns of samples with low carbon concentration. Regular shift of angular position of boron carbide peaks is observed with increasing of carbon concentration, whereas the position of silicon peaks remains unchanged. Patterns of samples with carbon concentration above 20 at.% exhibit a broad peak at \( 2θ \approx 26.4° \) which was attributed to free carbon formed in the final product at higher \( \sigma \). Other feature of XRD patterns is significant change of half-width of boron carbide peaks. It has a largest half-width at the carbon concentration of 13 at.%.
Figure 3 presents the main results of boron carbide investigation. The graphs show a non-linear dependence of lattice parameters on carbon concentration. Change in lattice parameters occurs in a different fashion (Fig. 3a and 3b): the drop for $a$ is 0.045 Å (about 1%), while for $c$ – 0.243 Å (about 2%). The increasing half-width of the lines changes with the rise of carbon content and approaches its maximum at $\sigma = 13$ at.% (Fig. 3d).

Obtained experimental data can be divided into 5 different regions (Fig. 3) where lattice parameters change similarly. Changes in the line half-width and lattice parameters reflect entrance of carbon atoms into boron carbide structure. At $\sigma \approx 13$ at.% the process of disordering takes place and after that (up to 18 at.%) the narrowing in half-width picks can be observed which indicates the ordering process in the structure.

In region I ($5.0 \leq \sigma \leq 10.8$) parameters $a$ and $c$ remains actually unaffected, at $\sigma > 7\%$ their decay and change of half-width lines get started.

In region II ($10.8 \leq \sigma \leq 13.2$) fast change in picks half-width is observed, carbide of composition $\text{B}_13\text{C}_2$ with probably maximal disordering structure corresponds to $\sigma = 13.2$ at.%

Region III ($13.2 \leq \sigma \leq 17.7$) is characterized as significant change in lattice parameters and diffraction lines compression which is indicative of transition of disordering process into ordering one.

In region IV ($17.7 \leq \sigma \leq 22.0$) a drop in lattice parameters slows down, free carbon appears, transition to stoichiometric composition $\text{B}_4\text{C}$ occurs and the process of ordering has been completed, which is evidenced by equal values for half-width of all boron carbide reflections.

Region V ($22.0 \leq \sigma \leq 30.0$). The observed slow decrease in the lattice parameters is indicative of possibly continuing introduction of carbon into the boron carbide.

In Fig. 3a, 3b, 3c our experimental results are given in comparison with literature data [1, 2, 3-15] where the spread is significant especially for $\sigma = 13$ at.%. Such spread is not typical for crystals of covalent bonds. SHS process provides more homogeneous conditions for crystal structure formation.
so our results (lattice parameters) demonstrate less spread in values. However in our data parameter $c$ has unusual high value in area of low carbon concentrations in boron carbide (Fig. 3b).

Figure 4 shows the fragment of the boron carbide lattice [5, 16] indicating four possible sites for replacement of boron by carbon. Taking into account the absence of C–C contacts in structure of boron carbide, incorporation of carbon atoms must be strictly ordered not only in one structural unit but also in the neighboring units.

A wide spread in the literature lattice parameters can be associated with incorporation of carbon atoms into different positions in both the linear groups and icosahedra. In other words, some certain composition can correspond to different structure.

Therefore, both experimental data and crystal-chemical considerations allow to conclude the possibility of different kinds of ordering in boron carbide structure, resulting in instability of lattice parameters and consequently in properties.

Conclusions

1. The monotonic dependence of lattice parameters on carbon concentration was established for SHS-production of boron carbide.
2. The correlation between half-width of diffraction lines and carbon concentration was established that probably reflects the phasic replacement of boron atoms by carbon ones in the boron carbide structure.
3. In literature the wide spread in values of lattice parameters for the same chemical composition was established. Considering four positions for the possible carbon incorporation into the structure, the spread in parameters can be explained by realization of different ways of carbon atoms ordering.
4. The described phenomenon of ordering in crystals with covalent bonds assumes possibility of realization of the certain ordering where change in properties can take place.

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