X-ray and EPR study of reactions between B$_4$C and TiO$_2$

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Abstract

X-ray diffraction and electron paramagnetic resonance (EPR) methods have been used to study the reaction process in a system of 95 wt.% of B$_4$C + 5 wt.% TiO$_2$. The addition of TiO$_2$ to B$_4$C was effective in accelerating the removal of carbon inclusions. Two types of reactions between B$_4$C and TiO$_2$, starting at temperatures ∼1173 K, took place: (a) gas-transport exchange and (b) diffusion of Ti atoms into the B$_4$C lattice. These reactions modify the number and type of donor centers in the B$_4$C. The dependence of EPR line width on the number of donor centers in B$_4$C (from conditions of sample treatment) is a useful method for investigating the formation of powders and ceramics based on B$_4$C.
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Keywords: Boron carbide; Titanium dioxide; Reactive sintering; Electron paramagnetic resonance (EPR); Carbon inclusions

1. Introduction

Reactive sintering of B$_4$C with the addition of different oxides (Al$_2$O$_3$, TiO$_2$, ZrO$_2$, etc.) is usually used for obtaining fully dense (higher than 80% of the theoretical maximum) composites [1–5]. Reactive sintering of the mixtures takes place at temperatures of 2173–2473 K. Reactions between B$_4$C and oxides (forming AlB$_2$, TiB$_2$, ZrB$_2$) promotes densification of boride ceramics during pressureless sintering as well as during hot pressing under pressure. For example, the proposed reaction between B$_4$C and TiO$_2$ to form TiB$_2$ is as follows [6]:

$$4B_4C(s) + 5TiO_2(s) = 5TiB_2(s) + 4CO(g) + 6BO(g). \quad (1)$$
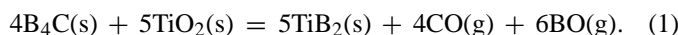
where (s) means solid and (g) means gas. Similar reaction mechanisms were confirmed by mass-spectrometry of the temperature dependence of the composition of a gas–vapor phase in mixtures of B$_4$C with different oxides other than TiO$_2$ [7]. It is observed that the most intensive out gassing of CO and BO (B$_2$O$_2$) takes place in the range 1173–1573 K [7]. Furthermore, formation of the boride phases of metals takes place at temperatures of about 1773 K [2]. Observation of various (intermediate) products of reaction (1) at different temperatures (much lower than sintering temperature) indicates a considerably more complex interphase interaction in such systems. Understanding the details of the

reaction "up to temperatures of sintering" is important in developing the technology of ceramics based on boron carbide B$_4$C.

In the present research, we shall discuss the evolution of chemical interactions in a dispersed mixture of B$_4$C–xTiO$_2$ during heat treatment by using electron paramagnetic resonance (EPR)-studies and X-ray analysis. We shall give special attention to determining the role of carbon inclusions in particles of B$_4$C in the formation of borides and to the reaction processes between atoms of Ti with molecules of B$_4$C.

In reference [8] it was concluded that for a typical EPR signal with $g = 2.0028$ the source is a type of radical B$_3$C$^\bullet$ with local concentration $N_{loc} \sim 10^{19} \div 2 \times 10^{20}$ cm^{-3}. The dependence of EPR line width (ΔB) on free carbon inclusions in B$_4$C was for the first time demonstrated in reference [9]. For arbitrary temperature, the EPR signal width (ΔB) is expressed by the formula [8]:

$$\Delta B(T) = \frac{b_1}{(1 + \alpha f(T))^{1/2}} + b_2 \cdot T \cdot \exp\left(\frac{-\Delta E}{kT}\right), \quad (2)$$

where $\alpha f(T) = (0.5 pm_2 \omega_c^2 / m_4)$—$m_2$ and m_4 are the second and the fourth moments for the static spectrum, which are typically determined by hyperfine and dipole–dipole interactions. p is the density of jump states at low temperatures. ω_c is a correlation frequency of the narrowing action of the spectrum. The second term in Eq. (2) describes the broadening of the EPR line with the temperature increase $T > 100$ K and this is the contribution of the "Korringa mechanism". ΔE is the activation energy for thermal generation of free charge carriers. Coefficient b_2

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is proportional to the square of the concentration of electron donor centers and to the square of the exchange-interaction value between the paramagnetic centers and free carriers [8].

In our analysis [10] the number of donor centers in boron carbide was associated with the surface carbon inclusions. We established that heat treatment (1 h at T_t from 873 to 1973 K) of boron carbide powders in low vacuum ($P \geq 1$ Pa) leads to a decrease in ΔB. These data permit us to conclude that all the changes found are due to the interaction of carbide powders with oxygen from the working atmosphere. Comparing the number of donor centers in B_4C with surface of carbon inclusions has allowed the authors to determine the difference of the surface to volume ratio (S/V) between carbon inclusions located in superficial layers and those carbon inclusions inside the particles of a powder [10].

As was noted above, in expression (1) the factor b_2 can be expanded as

$$b_2 \sim \left(\sum_i N_i\right)^2,$$

where N_i is the concentration of the donor centers of various natures. That is to say that EPR line width (see Eq. (2)) can serve as a sensitive indicator of either reduction or increase of the number of donor centers, irrespective of their nature. Such an approach was used in the present research to consider the mechanisms of chemical interaction in a system of $B_4C + x TiO_2$. In this case the reduction of carbon inclusions will promote narrowing of the EPR signal. At the same time, entry of Ti atoms into the lattice structure of B_4C should lead to an increase of the number of donor centers and promote the widening of the EPR line or signal.

2. Experimental procedure

Boron carbide powders were obtained by thermal reduction of B_2O_3 using carbon at $T_t = 2023$ K during $t = 4$ h in a hydrogen medium (chemical reagents from Baku, Azerbaijan). The specific surface of the powders was $S_{sp} = 1.1$ m^2 g^{-1}. Homogenous powders and also a mixture of 95 wt.% of $B_4C + 5$ wt.% TiO_2 (free filling, height 2 mm) powders were heated for 1 h at T_t from 873 to 1973 K, in low vacuum with pressures $P_1 = 1$ Pa and $P_2 = 2$ Pa.

Measurements of EPR spectra were made using Radiopan X-range radiospectrometer model SE/X 2547 (Poznan, Poland) over the temperature range 77–350 K. The phase composition of the powders was determined from an X-ray diffractometer (PW 1720, Eindhoven, the Netherlands, Cu Kα line).

3. Experimental results

Via X-ray diffraction it was determined that boron carbide B_4C was the main product of the thermal reduction (Fig. 1). The amount of free carbon (a graphite phase) in samples was measured via X-ray, using the method described in reference [11] and shown in Fig. 2. Authors [11] found that diffraction line (0 0 2) of graphite is present in the spectra of typical boron
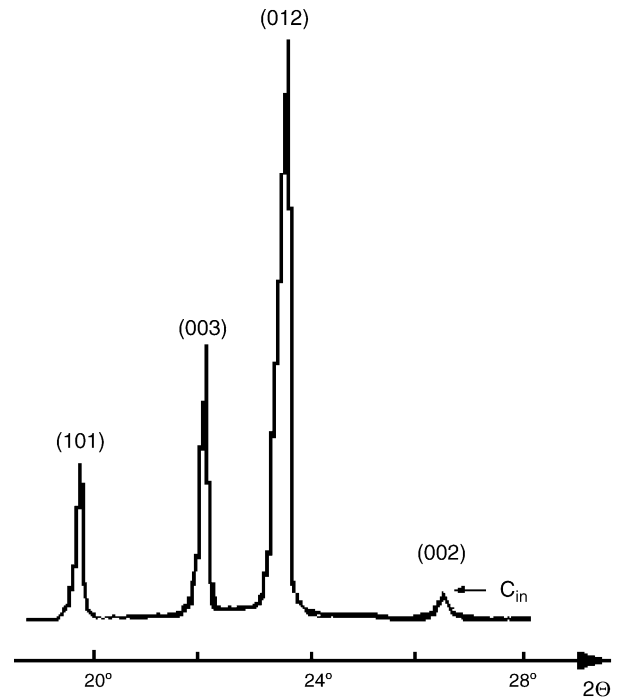

Fig. 1. X-ray diffraction pattern of initial B_4C powder. Line (0 0 2) is labeled by C_{in} and corresponds to a graphite phase of carbon inclusions.

carbide samples (see Fig. 1) and its intensity increases quite linearly with increasing concentration of free carbon as graphite, compared with the diffraction line (1 0 1) of boron carbide. This linearity holds quite satisfactorily up to 5% of free carbon [11].

X-ray data (Fig. 2) show that carbon inclusions in the B_4C powder begin to decrease at $T_t \sim 1173$ K. This decrease of carbon depends on both the air pressure in the thermal treatment chamber (see curves 1 and 2 or curves 3 and 4, Fig. 1) and on the presence of TiO_2 in the samples (see curves 1 and 3 or curves 2 and 4, Fig. 1).

A single EPR line of nearly Lorentzian shape with g-factor $g = 2.0028 \pm 0.0002$ was recorded for all samples (Fig. 3). The amplitude (A) and linewidth (ΔB—the distance between extreme points of the absorption line derivative) of the EPR signal depend both on the conditions of sample treatment and on the
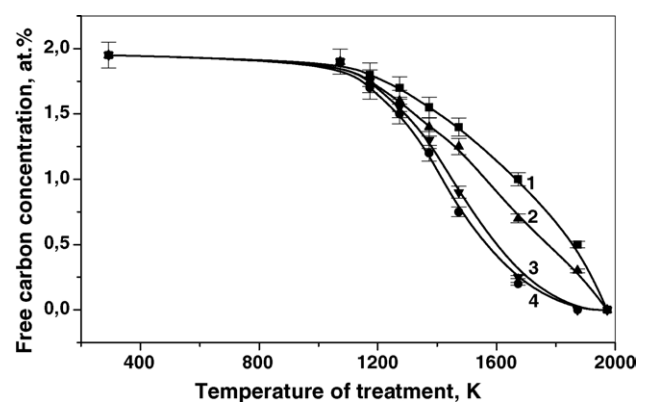

Fig. 2. The dependence of free carbon concentration in the samples B_4C (curves 1 and 2) and 95 wt.% of $B_4C + 5$ wt.% TiO_2 (curves 3 and 4) on the temperature of samples treatment. 1, 3, $P_1 = 1$ Pa; 2, 4, $P_2 = 2$ Pa.
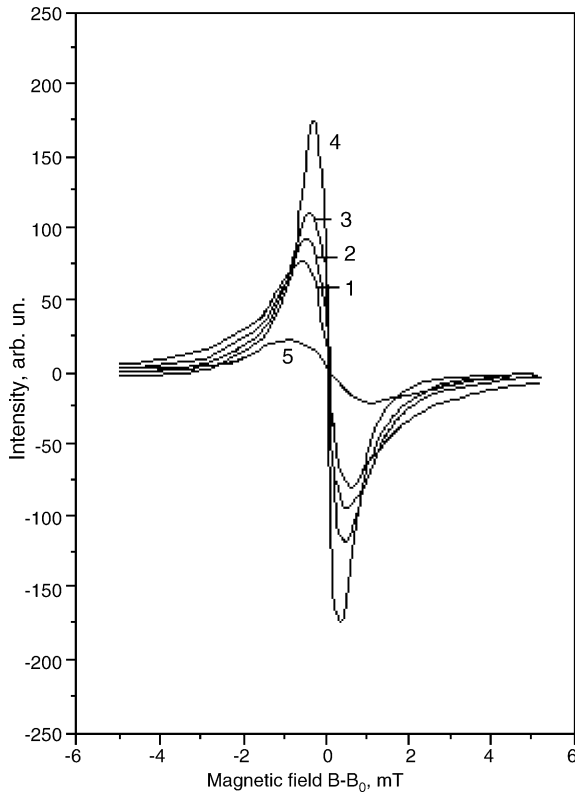
Fig. 3. The observed EPR-spectra (room temperature) for samples of clean B_4C (spectra 1, 2 and 4) and in mixtures of 95 wt.% of B_4C + 5 wt.% TiO_2 (spectra 3 and 5). 1, initial B_4C; 2, 3 at $T_t = 1373$ K, $P_1 = 1$ Pa; 4, 5 at $T_t = 1873$ K, $P_1 = 1$ Pa.

temperature of measurement. Fig. 4 shows the changes of EPR line width in samples of clean B_4C and in mixtures of 95 wt.% of B_4C + 5 wt.% TiO_2 which depend on temperature of processing, air pressure in the thermal treatment chamber (see curves 1 and 2 or curves 3 and 4, Fig. 4) and on the presence of TiO_2 in the samples (see curves 1 and 3 or curves 2 and 4, Fig. 4).

In clean B_4C samples the consequent reduction of $\Delta B(T_t)$ with increasing T_t, is observed and thought to be caused by oxidation of carbon inclusions. The reduction of $\Delta B(T_t)$ increases with increasing air pressure in the chamber (curves 1 and 2, Fig. 4).
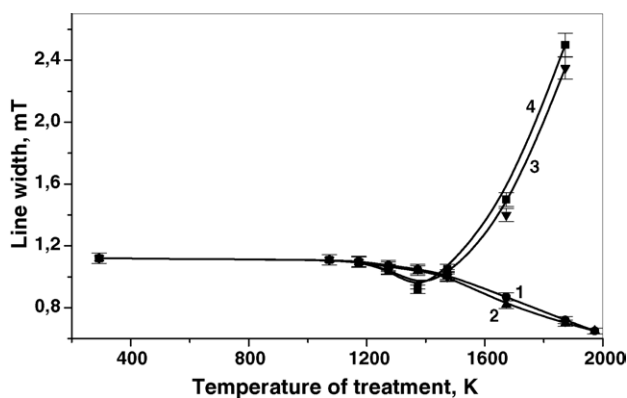

Fig. 4. The dependence of the EPR signal line width (room temperature) in the samples B_4C (curves 1 and 2) and 95 wt.% of B_4C + 5 wt.% TiO_2 (curves 3 and 4) on the temperature of samples treatment. 1, 3, $P_1 = 1$ Pa; 2, 4, $P_2 = 2$ Pa.
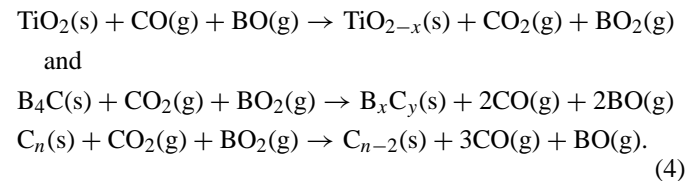
The change of $\Delta B(T_t)$ in samples of 95 wt.% of B_4C + 5 wt.% of TiO_2 mixture has a more complex character (curves 3 and 4, Fig. 4). Starting at $T_t = 1173$ K in these samples reduction also is observed, but the character of the reduction is sharper, than in samples of clean B_4C. $\Delta B(T_t)$ is at its minimal value after heat treatment at $T_t = 1373$ K. Further increase in T_t results in a sharp and intensified widening of the EPR line, $\Delta B(T_t)$ (curves 3 and 4, Fig. 4).

4. Discussion

The acceleration of the process of removal of carbon inclusions from the B_4C particles with addition of TiO_2 is most probably caused by oxygen formed by dissociation of TiO_2. Removal of included carbon in B_4C mixed with a powder of TiO_2 is accelerated by oxygen dissociated from TiO_2. One of the possible reactions of the dissociation of TiO_2 might be:

$$N(TiO_2) \rightarrow N(TiO_{2-x}) + N_xO(g). \tag{3}$$
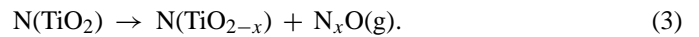
Reactions such as (1) and (3) can occur both in zones of contact between particles B_4C and TiO_2 and as a result of gas-transport reactions. A small amount of TiO_2 (5 wt.%) mixed into a sample of B_4C facilitates the oxidation of included carbon throughout the entire sample volume. We have also established that the TiO_2 dissociation process is accelerated by increasing the B_4C in a mixture of $(1-x)$ $B_4C + x TiO_2$. So after heat treatment of a clean powder of TiO_2 at $T_t = 1873$ K X-ray analysis shows the principal phase is rutile with traces of dissociation products of TiO_2 (Ti_3O_5 and Ti_2O_3). In the 5 wt.% B_4C + 95 wt.% TiO_2 samples after heat treatment at $T_t = 1873$ K the principal phase is Ti_2O_3. These data show that gas-transport reactions of B_4C oxidation and TiO_2 dissociation have exchanged character. For example,

$$TiO_2(s) + CO(g) + BO(g) \rightarrow TiO_{2-x}(s) + CO_2(g) + BO_2(g)$$
and
$$B_4C(s) + CO_2(g) + BO_2(g) \rightarrow B_xC_y(s) + 2CO(g) + 2BO(g)$$
$$C_n(s) + CO_2(g) + BO_2(g) \rightarrow C_{n-2}(s) + 3CO(g) + BO(g). \tag{4}$$

Note that included carbon can be completely eliminated from superficial layers and from the interior spaces of particles of B_4C by heat treatment ($T_t \sim 1173$–1973 K) in low vacuum [8]. We observed formation of a phase TiB_2 in samples 50 wt.% B_4C + 50 wt.% TiO_2 only after heat treatment of mixtures at $T_t \geq 1873$ K.

The EPR line width reduction in samples of clean powders of B_4C after heat treatment, depending on experimental conditions (Fig. 4, curves 1 and 2) was discussed by us earlier [8,10] and is caused by reduction of the quantity of carbon inclusions in the powders. Superficial atoms of carbon in the inclusions play the role of the donor centers for B_4C. It is natural to attribute the acceleration of $\Delta B(T_t)$ reduction to the acceleration of the oxidation of included carbon in mixed powder samples of 95 wt.% B_4C + 5 wt.% TiO_2 heat treated in a range $T_t = 1173$–1373 K (Fig. 4, curves 3 and 4). Subsequent ($T_t > 1373$ K) growth of $\Delta B(T_t)$ (Fig. 4, curves 3 and 4) is caused by invasion (diffusion)

of atoms of Ti into superficial defective layers of the particles of B_4C. Such atoms play the role of new donor centers. For the considered system it is possible to define that the general number of the donor centers in a sample, depending on temperature (T_t) and pressure (P) of processing, is the sum of the number of donor centers (N_{DC}) contributed both by carbon inclusions (N_C) and by the number of diffusing atoms Ti (N_{Ti}):

$$N_{DC}(T_t, P) = N_C(T_t, P) + N_{Ti}(T_t, P). \tag{5}$$

Therefore, taking into account Eqs. (2), and (5) the signal width for constant temperature of measurement is decribed by the formula:

$$\Delta B(T_t, P) = \Delta B_0 + \alpha[N_C(T_t, P) + N_{Ti}(T_t, P)]^2, \tag{6}$$

where ΔB_0 is signal width in case of sample without donor centers; α is coefficient depending on temperature of measurement. That is the change in ΔB can serve as a sensor for controlling the dynamics of the donor centers in samples B_4C depending on conditions (T_t, P and others) of processing.

5. Summary and conclusions

EPR- and X-ray diffraction methods were used to study the reaction process in a system of 95 wt.% of B_4C + 5 wt.% TiO_2. The addition of TiO_2 to B_4C was effective in accelerating the removal of carbon inclusions. Two types of reactions between B_4C and TiO_2, starting at temperatures ~1173 K, took place: (a) gas-transport exchange reactions, and (b) diffusion of Ti

atoms into the lattice of B_4C. These reactions modify the number and type of donor centers in the B_4C. The dependence of the EPR-line width on the number of donor centers in B_4C (from conditions of sample treatment) is a useful method for investigating the formation of powders and ceramics based on B_4C.

References

[1] M.D. Vlajic, V.D. Krstic, U.S. Patent No. 5,720,910, February (1998).
[2] L. Levin, N. Frage, M.P. Dariel, Metall. Mater. Trans. A 30 (1999) 3201–3210.
[3] H.-W. Kim, Y.-H. Koh, H.-E. Kim, J. Mater. Res. 15 (2000) 2431–2436.
[4] R. Telle, G. Petzow, Mater. Sci. Eng. A 105 (1988) 97–104.
[5] C.H. Lee, C.H. Kim, J. Mater. Sci. 27 (1992) 6335–6342.
[6] JANAF Thermochemical Tables, third ed., National Bureau of Standards, Washington, DC, 1985.
[7] G.N. Makarenko, V.B. Fedorus, S.P. Gordiyenko, V.M. Vereschak, E.V. Marek, O.F. Chernusheva, Powder Metall. Met. Ceram. 34 (1995) 447–451.
[8] M.G. Kakazey, J.G. Gonzalez-Rodriguez, M.V. Vlasova, B.D. Shanina, J. Appl. Phys. 91 (2002) 4438–4446.
[9] A. Bandyopadhyay, F. Beuneu, L. Zuppiroli, M. Beauvy, Phys. Chem. Sol. 45 (1984) 207–215.
[10] M. Kakazey, M. Vlasova, J.G. Gonzalez-Rodriguez, M. Dominguez-Patiño, R. Leder, J. Am. Ceram. Soc. 87 (2004) 1336–1338.
[11] M. Beauvy, R.J. Angers, Less Common Met. 80 (1981) 227–235.