Optimization of the obtaining temperature of powder composite material $B_4C – ZrB_2$ by the boron carbide method

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Abstract. Boron carbide is characterized by a unique combination of low density (2.52 g/cm^3), high hardness (up to 40 GPa), chemical inertness, the high melting point (2450 °C); for these reasons, the ceramics based on this compound have found application in a number of areas of state-of-the-art technologies. However, it is difficult to obtain dense B_4C-based ceramics because of a low value of the self-diffusion coefficient, low plastic deformation of this compound, and high sliding resistance between its grains. The use of modifying additives of transition metal diborides appears to be a promising approach to improving the operational characteristics of B_4C-based ceramics. They tend to activate the sintering process by means of activation energy reduction, which leads to a decrease in a grain size, an increase in density, strength, and fracture strength of sintered compositions. Zirconium diboride is often used for this purpose. The objective of the work is to study the changes occurring in the charge of boron carbide, zirconium dioxide and carbon when it is heated to determine the temperature of the complete reagents transformation into $B_4C – ZrB_2$ composite mixture.

1 Introduction

Boron carbide is characterized by a unique combination of low density (2.52 g/cm^3), high hardness (up to 40 GPa), chemical inertness, the high melting point (2450 °C). For these reasons, the ceramics based on this compound have found application in a number of areas of state-of-the-art technologies. However, it is difficult to obtain dense B_4C-based ceramics because of a low value of the self-diffusion coefficient, low plastic deformation of this compound, and high sliding resistance between its grains. The use of modifying additives of transition metal diborides is thought to be a promising approach to improving the operational characteristics of the ceramics based on B_4C. Their addition tends to activate the sintering process by reducing activation energy, which leads to a decrease in a grain size, an increase in the density, strength, and fracture strength of sintered compositions. Zirconium diboride is often used for this purpose. The following methods of manufacturing

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composite powders applied to prepare $B_4C–ZrB_2$ ceramics are possible: a) to mix boron carbide and zirconium diboride [3]; b) to mix boron, carbon and zirconium [4]. Both processes feature the need for thorough mixing of reagent before sintering. The need no longer exists with carbide-boron reduction of zirconium oxide in excess of boron carbide, since the formed particles of zirconium diboride will be uniformly distributed within boron carbide matrix. Information on the approach to preparation of charge materials from boron carbide and zirconium diboride is not available in the literature.

The objective of this research is to study the changes occurring in the mixture of boron carbide, zirconium dioxide and carbon when it is heated to determine the temperature of complete conversion of the reagents.

2 Experimental

Composite powder with a composition (mol %) of 75 B_4C and 25 ZrB_2, was prepared by reaction (1):

$$7B_4C + 2ZrO_2 + 3C = 2ZrB_2 + 6B_4C + 4CO \qquad (1)$$

The experiments were carried out in an induction crucible furnace, in an argon atmosphere to prevent undesirable nitriding of boron carbide and resulting zirconium diboride. The synthesis duration was 20 minutes for all the samples. The pressure in the reactor was close to atmospheric. It was impossible to determine the partial pressure of carbon monoxide in the gas mixture (Ar and CO) under these conditions. Therefore, the temperatures of the reduction onset were determined for different CO pressures. The results of thermodynamic calculations are shown in Fig. 1.

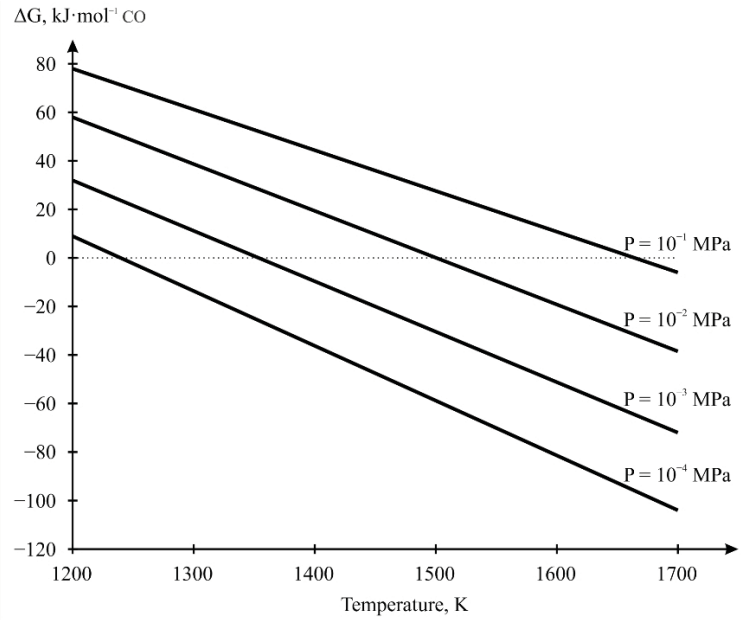

Fig. 1. Temperature dependence of the isobaric-isothermal reaction potential under carbide-boron reduction of zirconium dioxide at different CO pressures.

Consistent with the analysis data of the value of the isobaric-isothermal reaction potential for carbide boron reduction at different CO pressures, MPa: 0.0001; 0.001; 0.01 and 0.1, it follows that the reduction onset temperatures fall in the range: 1240, 1340, 1510 and 1660 K. To complete the reaction of boride formation, higher temperatures could be set. According to thermodynamic modelling data, complete conversion of reagents into target compounds occurs at temperatures above 1540 °C [5]. The heat treatment of the charge materials was carried out at the temperatures, °C: 1000, 1200, 1400 and 1650.

The reaction behavior degree was assessed during the synthesis of the samples by the change in the mass of the sample after the synthesis and by comparison of the obtained value with the theoretical one. The analysis represents the full course of the synthesis reactions. The phase composition of the obtained composite mixtures was determined by the X-ray phase method with a diffractometer under Cu Kα radiation. Scanning electron microscopy (SEM) was applied to study the surface morphology and particle size.

3 Results and discussion

In this study, the high-temperature synthesis of composite powder materials containing 25 mol% ZrB_2 and 75 mol% B_4C was carried out at different temperatures, °C: 1000, 1200, 1400 and 1650. The completeness of the reaction course was estimated according to the weight loss data. The calculated weight loss with the complete course of the reaction is 16.62 wt. %. Data on the actual weight loss are presented in Table 1.

Table 1. The results of the experiments on the synthesis of powder materials with the composition, mol%: $75B_4C$-$25ZrB_2$; the reaction took place at various temperatures.

Synthesis temperature, °C	Charge materials weight, g	Mass of solid reaction products, g	Weight loss, g	Actual weight loss, %
1000	3.125	3.098	0.027	0.86
1200	3.103	3.062	0.041	1.32
1400	3.289	3.212	0.077	2.34
1650	12.721	10.749	1.972	15.50

Consistent with the results (Table 1), it follows that the boride formation reaction starts at 1000 °C, but it is completed at 1650 °C.

X-ray phase analysis was carried out to determine the phase composition of the powder composite materials obtained at different temperatures. The diffraction patterns of the samples are shown in Fig. 2. The analysis of the diffraction patterns reveals that the peaks of unreacted ZrO_2 and C phases are clearly visible at synthesis temperatures of 1000 and 1200 °C, but only insignificant peaks corresponding to the ZrB_2 phase are seen. The peaks of the ZrO_2 phase are still present in the diffractogram at a synthesis temperature of 1400 °C. However, clear presence of ZrB_2 and B_4C target phases is evident. The process is completed at 1650 °C, and only the peaks of the target phases are shown in the diffractogram.

Scanning electron micrographs of the powder materials samples synthesized at 1000, 1200, 1400 and 1650 °C are shown in Fig. 3. One can observe the presence of non-uniform particles, and some of them are fragmented on the samples obtained at 1000, 1200 and 1400 °C (Fig. 3).

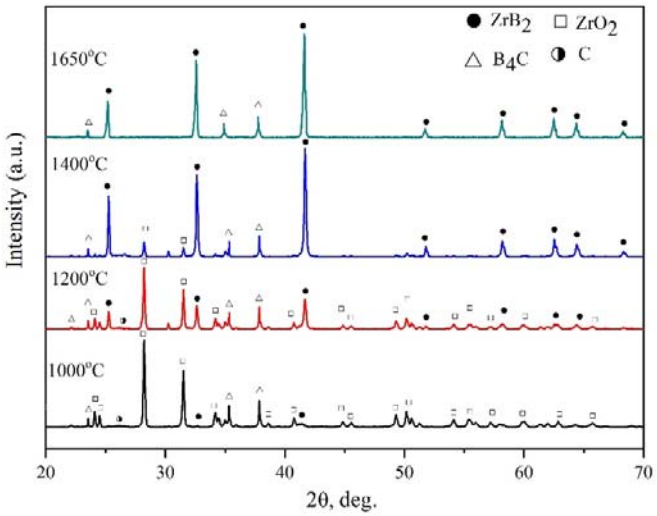

Fig. 2. Diffraction patterns of B_4C-ZrB_2 powder material samples synthesized at different temperatures.

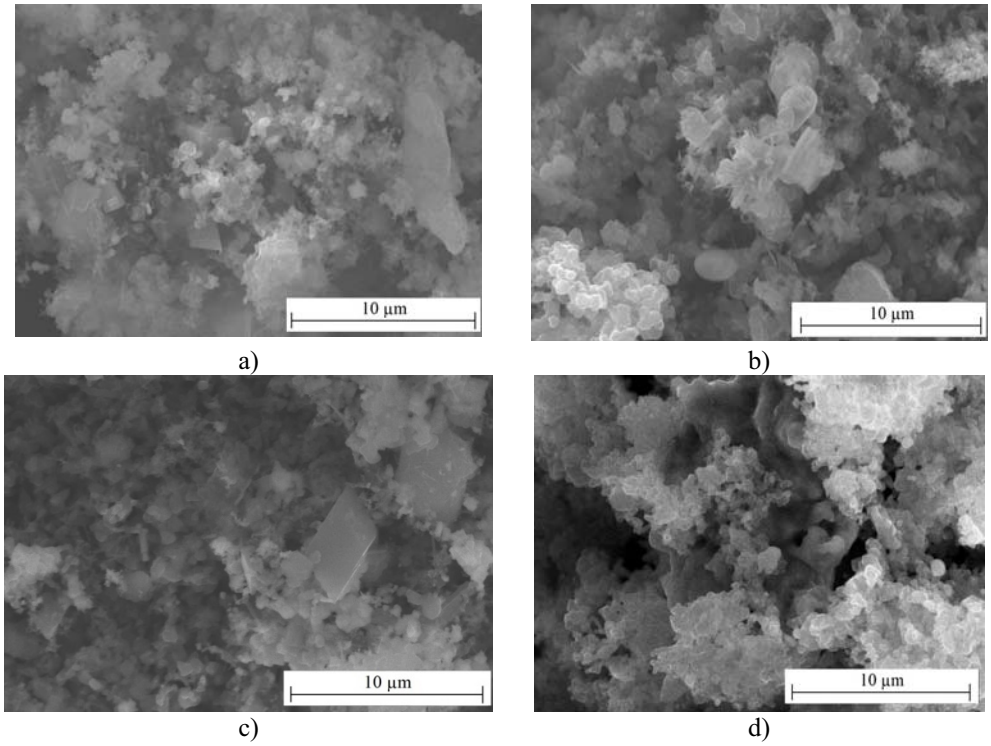

Fig. 3. SEM images of B_4C-ZrB_2 powder materials synthesized at temperatures, ° C: 1000 (a), 1200 (b), 1400 (c), 1650 (d).

4 Conclusion

High-temperature synthesis of B_4C – ZrB_2 composite powder material was carried out by the method of carbide-boron reduction of zirconium oxide at temperatures, °C: 1000, 1200, 1400 and 1650. The data on weight loss, X-ray phase analysis and scanning electron microscopy allowed us to determine the optimum temperature (1650 °C) to produce the composite powder of boron carbide - zirconium diboride by carbide-boron reduction of zirconium dioxide. The experimental data are in good agreement with the calculated ones and obtained by thermodynamic modeling. Complete conversion of reagents into target compounds occurs at temperatures above 1540 °C.

The work was performed in accordance with the State Order of the Ministry of Education and Science (FSUN-2020-0008 code).

References

1. X. Zhang, H. Gao, Z. Shang, R. Wen, G. Wang, J. Mu, H. Che, Ceram. Int. **43**, 6345 (2017)
2. W. Zhang, S. Yamashita, H. Kita, Adv. Appl. Ceram. **118**, 222 (2019)
3. Z. Mestvirishvili, I. Bairamashvili, V. Kvatchadze, N. Rekhviashvili, J. Mater. Sci. Eng. **5**, 385 (2015)
4. V.A. Shcherbakov, A.N. Gryadunov, A.I. Alymov, Letters on Materials **7**, 398 (2017)
5. V.A. Shestakov, T.S. Gudyma, Yu.L. Krutskii, N.F. Uvarov, Mater. Today: Proc. **31**, 3 (2020)