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Sintering of Boron and Boron Carbide

G. I. Kalandadze,* S. O. Shalamberidze,* and A. B. Peikrishvili†

**The Institute of Stable Isotopes, 21, Kavtaradze str., 380086 Tbilisi, Georgia; and †The Institute of Mining Mechanics, 7, Mindeli str., 380086 Tbilisi, Georgia*

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An investigation of sintering kinetics of boron and boron carbide is presented. The influence of the powder size distribution on the temperature dependence of sintering, on reaching a high final density, and on gaining a homogeneous grain size has been shown. The results on the α-rhombohedral usage in reaction sintering for boron carbide production have been given. With the example of boron, the maximum sintering density was reached as the process was managed under the conditions providing the successive phase transitions in boron, $B_{amorph.} \rightarrow B_{\alpha} \rightarrow B_{\beta}$. The results of sintering of boron and boron carbide pellets compacted by explosive compression have been considered. Explosive pressing–sintering produces pellets of amorphous and α-rhombohedral boron. © 2000 Academic Press

Key Words: **boron; Boron carbide; sintering; hot compacting; explosive compression.**

INTRODUCTION

Boron carbide and boron are neutron absorbers. They are hard to sinter due to their rigid covalent bonds and corresponding low diffusion mobility. The ways of pellet formation and sintering of these materials have regularly been of interest at previous symposiums on boron, borides, and related compounds (1–7).

This paper contains findings on the effect of the powder size distribution on boron carbide sintering parameters and the structure of the sintered body, on the boron carbide reactive sintering activated by phase transformations from α-rhombohedral, and on sintering the explosively compacted boron materials.

The obtained results sometimes differ from the previous data published by other investigators. An attempt to reinterpret these results has been made.

EXPERIMENTAL

Pyrolytic and electrolytic amorphous boron powder with a purity of 99.9 wt% and 96 wt% accordingly was used in this investigation. α- and β-rhombohedral boron was produced from amorphous boron by crystallization at temperatures 1200 and 1800°C, respectively. Boron carbide was produced by a direct synthesis from the elements at temperature 2000°C. The pellets were hot pressed at temperatures 1900–2100°C and pressures 20–40 MPa in boron nitride lined graphite moulds using resistance and inductive heating.

Shock compression, as a result of an explosive detonation, was realized in specialdesign ampoules. The powders were pressed in these ampoules up to 30% of a theoretical density. During the explosion the air was discharged as the shock wave transmitted. By varying a number of the parameters (ampoule geometry, the initial density of compressed material, the rate of a shock wave propagation, the preheating temperature, the choice of an explosive), it was possible to reach pressures up to 10 GPa.

The structure of the powders of the specified materials was examined with the DSM-50 scanning electron microscope, and the powder size distribution was studied with the LEITZ-TAS device.

RESULTS AND DISCUSSION

The morphology of different origin powders has been characterized by electron microscopic investigations (Fig. 1) and their particle size distributions are shown in Figs. 2a and 2b. The particle size distribution of these powders depends entirely on their production method. There was the opportunity to change (to extend or narrow) it by means of classifying.

It is well known that sintering rates, a final density, and the structure of sintered solids depend on the particle size distribution and the morphology of powder particles. Figure 3 shows the microstructures of hot-pressed boron carbide, illustrating homogeneous and inhomogeneous grain size resulting from monodisperse and polidisperse powders. The experimental data confirm the possibility of reaching higher densities from monodisperse powders, which is of particular importance in pressureless sintering. At the same time, it should be emphasized that the pellets from the monodisperse powders were produced at lower

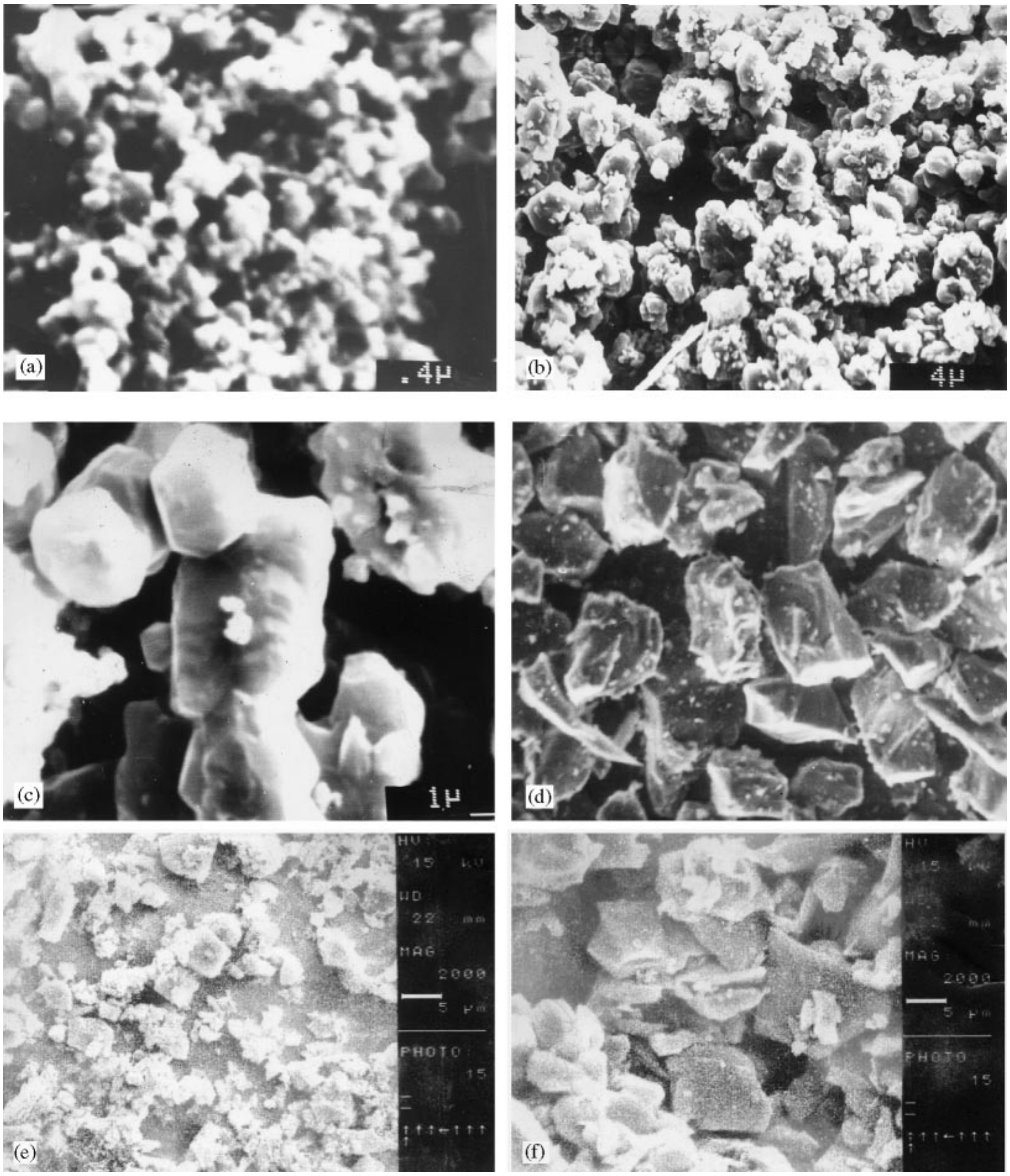

FIG. 1. Different powders: (a) pyrolytic amorphous boron, (b) electrolytic amorphous boron, (c) boron of α-rhombohedral modification, (d) boron of β-rhombohedral modification, (e) boron carbide-1, (f) boron carbide-2.

temperatures. Higher temperatures cause a great number of twins and grain size inhomogeneity due to grain growth.

Reactive sintering, i.e., sintering combined with synthesis under hot pressing is one of the conventional methods of boron carbide pellet production. As is known mass transport in reaction of boron and carbon powder mixtures depends on various conditions. The boron–carbon reaction takes place by directed mass transport, i.e., a preferred boron diffusion into carbon (8, 9), and carbon dispersity is determinative for the structure of the sintered pellet. The combination of synthesis (1250–1500°C) and sintering (1800–2200°C) in the same process gives certain advantages of temperature conditions. Owing to an isostructural character of α-rhombohedral boron and boron carbide the advantage becomes great when α-rhombohedral boron and carbon are mixed. Figure 4 shows the relative density dependence on the hot-pressing temperature for the powder mixtures (α-boron + C) and (B_{amorph} + C). The former mixture starts to be compacted at 1300°C and gradually increases in density until the maximum value is reached at 1800°C. The latter mixture (B_{amorph} + C) starts sintering at 1600°C and finishes at 2050–2100°C.

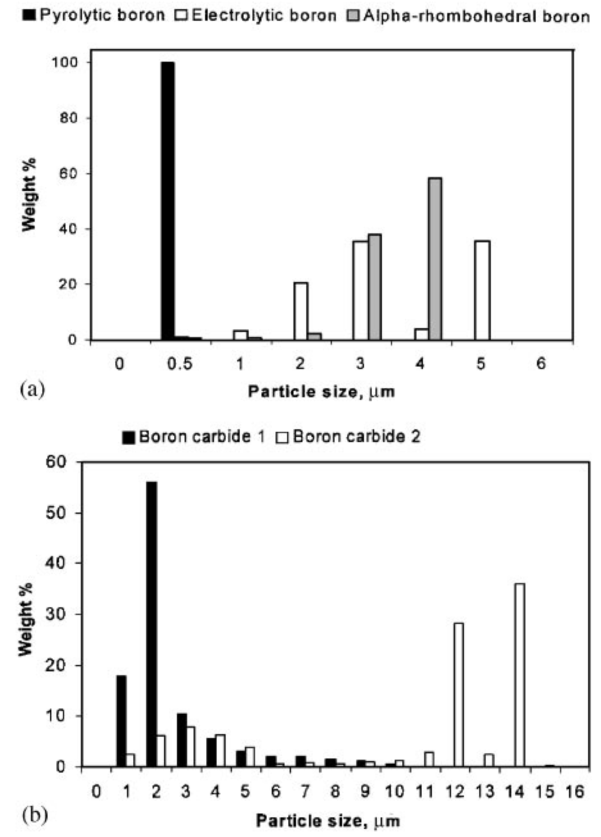

FIG. 2. Particle size distribution: (a) boron powders, (b) boron carbide powders.

Powder metallurgy requests the usage of fine powders for the improved sintering and density rise. According to (10), to raise the relative density from 35 to 62% during sintering at 2100°C (1 h, helium atmosphere), the mean size of amorphous boron powder must be 0.036 μm. According to (7), no density change occurred during vacuum sintering of β-rhombohedral boron powder pellets of mean particle diameter 9 μm at temperatures 1800–1950°C. An increase in interparticle contacts and the specific surface change, however, were detected. Our investigations (11) indicate that when a pellet of β-rhombohedral boron powders (average powder size 2 μm, specific surface 1.2 m^2/g, 35% initial porosity) was sintered pressureless for 2 h at 1960°C in argon, a 15% porosity was reached. The process kinetics was determined by the powder size and the lattice distortion degree as well as the degree of cold precompacting. By the suggested (10) ratio $D/\mu \geq 4 \times 10^{-6}$ cm/s (D, self-diffusion factor; μ, particle size), the requirements as to the particle size of covalent bonded materials can be satisfied in the area of nanopowders (0.5 × 10^{-3} μm). Table 1 contains the data on hot pressing of boron having different forms: α- and β-rhombohedral boron and amorphous boron. The sintering conditions were chosen coincidently to all familiar phase transitions (12, 13) in amorphous and α-rhombohedral

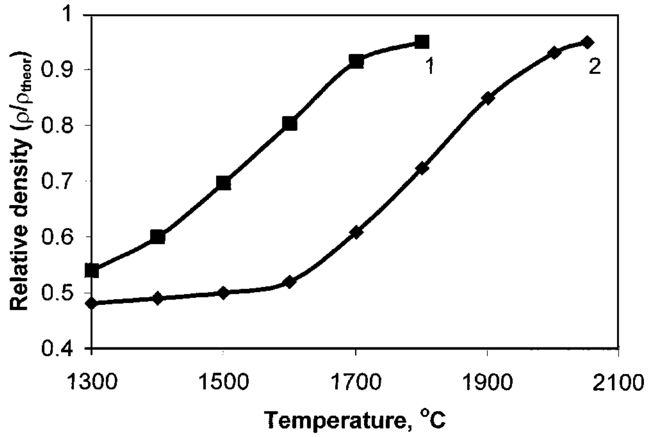

FIG. 4. Relative density vs hot pressing temperature for mixtures: (1) $B_\alpha + C$, (2) $B_{amorph} + C$.

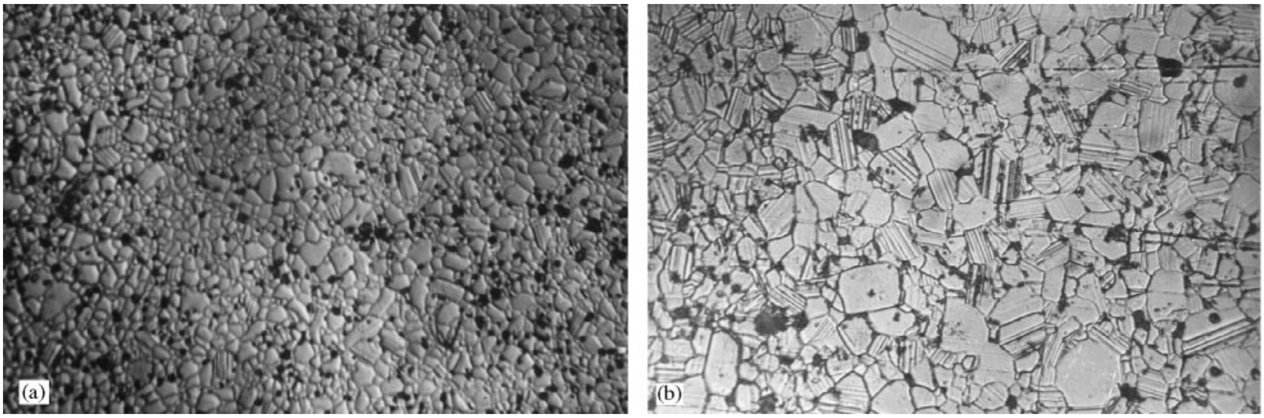

FIG. 3. The microstructure of hot-pressed boron carbide: (a) from monodisperse powder (× 300), (b) from polydisperse powder (× 300).

TABLE 1
Data on Hot-Pressed Boron Pellets

Initial powders	β-rhombohedral boron	Amorphous boron	α-rhombohedral boron
Grain size and specific surface	2 μm, 1.27 m^2/g	0.2 μm, 12.76 m^2/g	2.74 μm, 0.89 m^2/g
Initial pressure (MPa)	15	15	15
Heating rate (°C/min)	50 (up to 1950°C)	5 (950–1200°C) 20 (1200–1650°C) 50 (up to 950°C and over 1650°C	20 (950–1650°C) 50 (up to 950°C and over 650°C)
Final pressure (MPa)	30	30	30
Final sintering temperature	1950°C	1800°C	1800°C
Final phase	β-Rhombohedral	β-Rhombohedral	β-Rhombohedral
Final density (% of theoretical)	87%	99%	91%

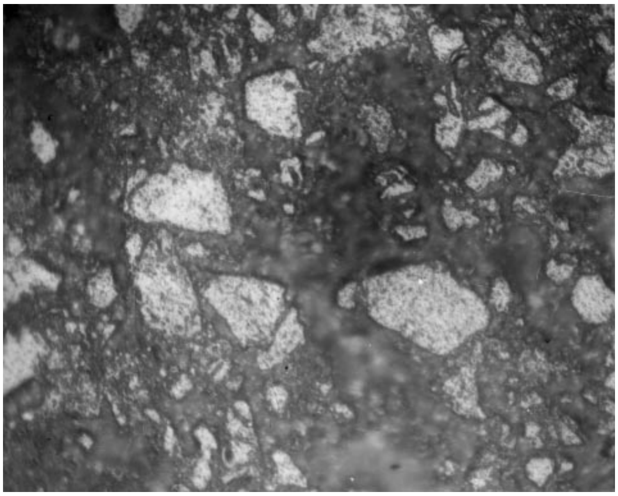

FIG. 6. Boron carbide (× 500) after the explosive compression and thermal treatment at 800°C.

boron (the phase transitions: amorphous $\rightarrow \alpha \rightarrow \beta^{I} \rightarrow \beta^{II} \rightarrow \beta$), which enhances sintering. This phenomenon, called the Hedvall effect, manifests itself in solid-state activity rise as a result of phase transformations. The obtained results show that better sintering property can be achieved as follows: $B_\beta \rightarrow B_\alpha \rightarrow B_{amorph}$. At the final stage, all modifications of boron transform to the β-rhombohedral modification, which is the only stable form at high temperatures.

At the same time the consolidation of the pellets of low-temperature boron modifications is of great scientific and practical interest. The possibilities of achieving high density using static and isostatic pressing are limited. Explosive compression turned out to be more promising. Figure 5 presents the hard-to-etch structures of the explosive compacted pellets of α-rhombohedral and amorphous boron. The pellets hold the initial phase. Even at densities over 98% of theoretical, no cohesion of powder particles occurred in the pellets. The pellets made by explosive compacting were subsequently sintered at considerably low temperatures: boron carbide at 1600°C and amorphous and α-rhombohedral boron at 1000 and 1200°C, respectively (below the temperature of a phase transformation). A thermal treatment for 10 min was quite sufficient to diminish the remaining micropores after the explosive compression and for grains to grow together. It was previously reported (14) that an explosive compression of boron may form defects and structure distortions favoring the activation of subsequent sintering. Even intermediate thermal treatment at 800°C facilitates to etch and detect individual grains (Fig. 6). A thermal treatment under the above-mentioned conditions forms the structures presented in Fig. 7.

CONCLUSION

Some problems of sintering of boron carbide as well as different modifications of boron have been investigated. The

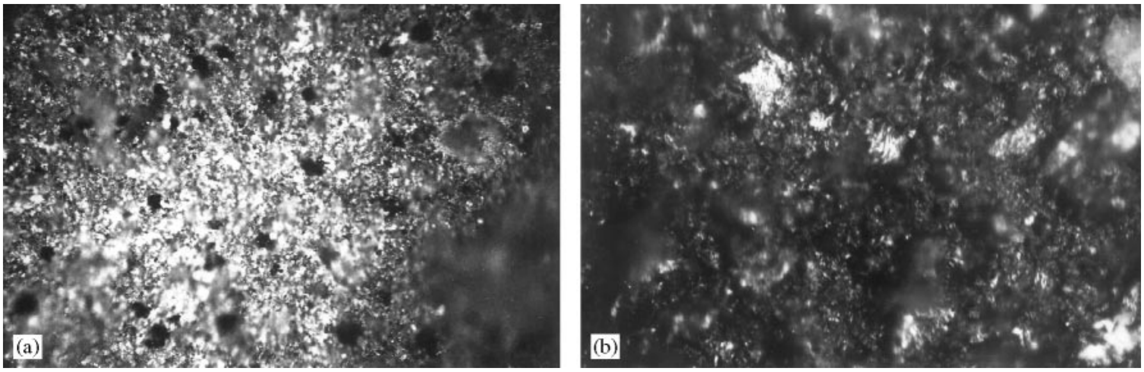

FIG. 5. α-Rhombohedral (a) and amorphous (b) boron (× 300) after the explosive compression.

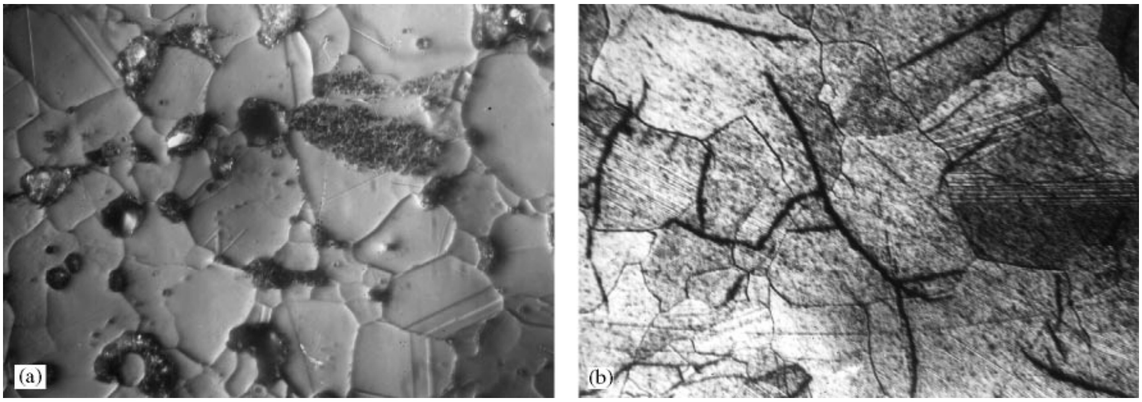

FIG. 7. (a) Boron carbide (× 800) after the explosive compression and thermal treatment at 1600°C; (b) α-rhombohedral boron (× 800) after the explosive compression and thermal treatment at 1200°C.

powder size distribution of boron carbide was found to determine the microstructure of a sintered pellet. The usage of α-rhombohedral boron to produce boron carbide pellets in reactive sintering could lower the maximum sintering temperature to 1800°C due to its isostructural character.

A comparison between α-rhombohedral, β-rhombohedral, and amorphous boron sintering property indicates that their sintering into the β-rhombohedral phase at the final stage can give higher densities as follows: $B_\beta \rightarrow B_\alpha \rightarrow B_{\mathrm{amorph}}$, which is attributed to the phase transformation occurrence from amorphous boron to β-rhombohedral boron through α-rhombohedral boron modification.

Explosive compacting and subsequent sintering of boron and boron carbide were performed. The absence of interparticle cohesion by explosive compacting as well as the occurrence of the interparticle cohesion after a short thermal treatment was detected.

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