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Composition Effects on the Microstructure and Mechanical Properties of Sintered Boron Carbide

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Abstract. Boron carbide is a remarkable material among those with high hardness. This work presents the results obtained after sintering a commercial B_4C powder with $C+B_2O_3+Al_2O_3$ and Ni, Ti, Ni+Ti, used as sintering aids. The effects of sintering aids on several parameters as sintering temperature, phase formation, microstructure, fracture toughness (K_{ic}) and microhardness (H_v) are also studied.

INTRODUCTION

Boron carbide (B_4C) is an interesting material with high melting point, very high hardness, low specific weight, good mechanical properties and high neutron absorption cross-section. The main applications are as abrasives, cutting tools, lightweight armors and neutron absorber. Moreover the use of B_4C components is limited by sintering difficulties due to the strong covalent bonding. The production of high density B_4C components by hot pressing requires pure and fine powders (<2 μm), high temperatures (2373-2473 K) and pressures in the range of 30-40 MPa within a pressing step from 15 to 45 min in a graphite die [1]. An alternative way is to use sintering aids that allow for a high degree of densification in the temperature range of 2023-2173 K [2, 3]. Small size and simple shape components may be obtained by hot pressing. More complicated shapes and larger sizes require different conformation techniques followed by sintering. The reliability of sintering B_4C is only possible with sintering aids such as Al, Mg, TiB_2, AlF_3, Ni, Fe, Cu and Be_2C [3-7]. Nevertheless the best results were obtained with carbon produced from "in situ" pyrolysis of phenolic resin (Novolaque type phenol-formaldehyde resin) [7-12]. In this case, 98% of the theoretical density was achieved at 2323 K under argon atmosphere.

The present work comprises a study regarding sintering of a commercial B_4C powder with $C+B_2O_3+Al_2O_3$ and Ni, Ti, Ni+Ti used as sintering aids in the temperature range of 1973-2473 K.

MATERIALS AND METHODS

Six kinds of raw materials were used for the studied compositions (Table 1), as follows:

- Boron carbide powder F-1200, from HCST (Hermann C. Starck);
- Phenolic resin as carbon source;
- Alumina BACO (G450), from Union Carbide Co.;
- Boron oxide P.A., from Merck;

- Nickel powder P.A., from Fisher Scientific Company;
- Titanium powder obtained from $TiCl_4$ through the "Kroll process" at the Materials Division of IAE/CTA (Brazil).

The steps for the preparation of those compositions are given below:

- Uniaxial pressing in a metal die under 40 MPa;
- Mixture of raw materials;
- Cold isostatic pressing under 300 MPa;
- Cure of resin in an oven at 473 K (BCAl composition);
- Resin carbonization at 1273 K, under purified Argon;
- Sintering under purified argon in the temperature range of 1973 - 2473 K, depending on the selected composition.

Table 1-Selected Compositions.

COMPOSITION	RAW-MATERIALS					
	B_4C	C	B_2O_3	Al_2O_3	Ti	Ni
BCAl	82.64	4.33	4.36	8.67	-	-
BTiNi-O1	89.39	1.80	-	-	8.37	0.44
BTiNi-02	83.14	1.80	-	-	0.75	14.31
BTiNi-03	88.33	1.80	-	-	7.07	2.80
BTi	89.59	1.80	-	-	8.61	-
BNi	82.53	1.80	-	-	-	15.67

The relative density ρ was determined by the Archimedes method. A picnometer was used for real density determination according to the ASTM specification. Scanning Electron Microscopy (SEM) and EDS analyses were useful techniques for microstructural evaluation. Vickers microhardness (H_v) and K_{ic} were measured by the indentation method, the specimens being polished up to 1μm diamond paste, a 19.6 N load was applied. K_{ic} was calculated from the following equation:

$$K_{ic} = 0.07626\ P / C^{3/2} \quad (1)$$

RESULTS

i) BCAl composition

The influence of Al_2O_3, B_2O_3 and carbon as sintering aids for B_4C was evaluated. Alumina reacts with B_2O_3 at low temperatures forming a liquid phase. Table 2 shows the variation of the density and microhardness values with sintering conditions. In this case we have the following results:

- A small densification occurs at 1973 K followed by a fast densification close to the 2223 to 2273 K range. The relative density values vary from 76% to 91%, reaching 97% of the theoretical density at 2373 K. The material melts at 2473 K.
- High hardness (21.0 GPa) was determined at 2373 K. The K_{ic} values indicate the low fracture toughness of these materials.

Fig. 1 shows the fracture surface of a material sintered at 2373 K for 1 hour. An intercrystalline fracture can be seen, as well as grains recovered by a possibly liquid phase. X-ray diffraction analysis shows the presence of B_4C, graphite, Al_2O_3 and $Al_{18}B_4O_{33}$; in the material sintered at 2273 K only B_4C, graphite and Al_2O_3 could be determined. It is assumed that a liquid phase was formed, without recrystallyzation during the cooling step. In fact, that might explain the high densification when the temperature increased. Another possibility is that a small quantity of $Al_{18}B_4O_{33}$ is not detected by X-ray diffraction technique.

Table 2-Variation of density, microhardness and K_{ic} with sintering conditions

Sintering conditions	Relative density [%]	H_v [GPa]	K_{ic} [MPa $m^{1/2}$]
1973 K/1h	60	-	-
2223 K/1h	76	-	-
2273 K/1h	91	16.0	4.1
2373 K/1h	97	21.0	3.5
2473 K/1h	melted	-	-

ii) The Use Of Ni and Ti as Sintering Aids.

Table 3 shows crystalline phases determined by X-ray diffraction:

- In Ti-rich compositions this element reacts with boron and carbon to form TiB_2 and TiC. The TiB_2 formation leads to a high densification degree for sintering temperatures in the 2423 to 2523 K range. It is possible to achieve up to 99% of the theoretical density when TiB_2 is used as sintering aid [4];
- In the material produced with Ti-rich compositions and also in the BNiTi-03, no Ni-phase was observed. Therefore Ni might be either in solution, in an amorphous state, or as a low content crystalline phase. In Ni-rich materials this element reacts with B_4C to form Ni_4B_3. Unreacted Ni was not detected in BiTiNi-02 composition;
- Free carbon under graphite form was detected in all compositions;
- Nickel carbide was not detected, therefore the resulting carbon from the reaction between Ni and B_4C might be either in solution or in a graphite state;

Table 4 shows relative density values and mechanical property parameters for different compositions and temperatures. The results showed that:

- Nickel is more effective sintering aid than titanium;
- A proportionality was observed between both microhardness and relative density values. When the nickel content is high, higher density and K_{ic} values were observed;
- A large dispersion was observed among K_{ic} values. Porous materials showed higher K_{ic} values. Nickel rich samples showed coherent K_{ic} values with these type of materials.

The material with BNi composition showed a compact microstructure (Fig. 2). Retained pores with 2-5μm in diameter may be observed. On polished surfaces (Fig. 3A) agglomerates

formed during the processing stage can be seen. Different shrinkage rates between their agglomerates and the matrix create defects. A bright phase can also be seen. EDS analysis showed high Ni content within this phase (Fig. 3B). XRD studies show Ni_4B_3 in the phase and filling the pores (Fig. 4). The sintering step was accelerated by this liquid phase leading to the densification of that material.

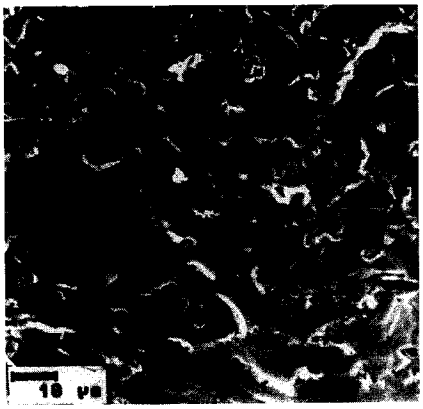


Fig.1-Scanning micrograph. Fracture surface of a BCAl material sintered at 2373K.

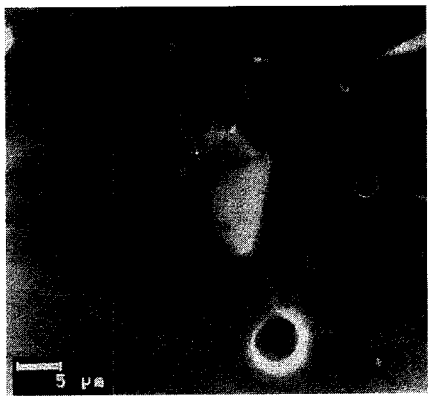
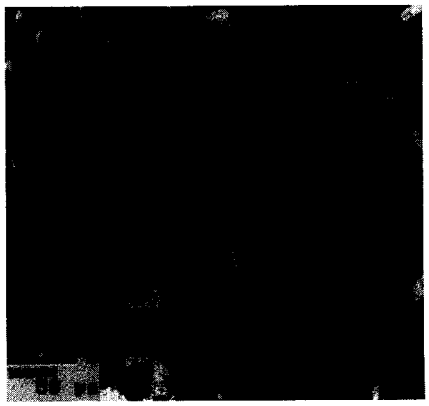


Fig.2-Scanning micrograph. Fracture surface of a BNi material sintered at 2373K

(A)



(B)

Fig. 3- SEM/EDS analysis of BNi material. (A) Secondary electron image, (B) X-ray image, $Nik_{\alpha 1}$

Table 3- Crystalline phases determined after sintering at 2373K in B_4C with Ti and/or Ni sintering aids.

Composition	Detected Phases (by XRD)
BTiNi-01	B_4C - TiB_2 - TiC - graphite
BTiNi-02	B_4C - TiB_2 - graphite
BTiNi-03	B_4C - TiB_2 - graphite
BTi	B_4C - TiB_2 - TiC - graphite
BNi	B_4C - Ni_4B_3 - graphite

Fig.4- Scanning micrograph. Polished and etched surface of BNi sintered at 2373K

Table 4- Variation of relative density and mechanical properties with both composition and temperature when Ni and/or Ti were added to the material.

Composition	Sintering temperature [K]	Relative density [%]	H_V [GPa]	K_{ic} [MPa.m$^{1/2}$]
BTiNi-01	1273	64	-	-
BTiNi-01	2173	57	-	-
BTiNi-01	2323	71	-	-
BTiNi-01	2373	71	6.0	5.2
BTiNi-02	1273	58	-	-
BTiNi-02	2173	71	-	-
BTiNi-02	2323	78	-	-
BTiNi-02	2373	84	18.2	3.2
BTiNi-03	1273	61	-	-
BTiNi-03	2173	57	-	-
BTiNi-03	2223	69	-	-
BTiNi-03	2373	80	16.3	3.6
BTi	1273	60	-	-
BTi	2173	62	-	-
BTi	2373	75	12.6	4.1
BNi	1273	60	-	-
BNi	2173	67	-	-
BNi	2373	95	23.7	2.9

CONCLUSIONS

The use of $C+B_2O_3+Al_2O_3$ as sintering aids is effective for sintering of BCAl composition. The mechanism may be understood as the "in-situ" reaction among Al_2O_3, B_2O_3 and C, with the formation of B_4C and $Al_{18}B_4O_{33}$. The densification was not improved by Ti adding, for sintering temperatures up to 2373 K.

Nickel is an effective sintering aid for B_4C. It is possible to reach a value of 95% of the theoretical density and a microhardness value of 23.7 GPa, when the material with BNi composition is sintered at 2373 K. BNi composition material showed a typical microstructure obtained from a liquid phase sintering process. Such liquid phase crystallizes as Ni_4B_3 and the maximum densification rate is in the temperature range of 2323 - 2373K.

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