ELSEVIER

Ceramics International 32 (2006) 227–233

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Pressureless sintering of boron carbide

T.K. Roy, C. Subramanian *, A.K. Suri

Materials Processing Division, Bhabha Atomic Research Centre, Mumbai 400085, India

Received 27 August 2004; received in revised form 10 January 2005; accepted 14 February 2005
Available online 22 April 2005

Abstract

The processing of boron carbide by pressureless sintering with and without additives to obtain dense pellets for use as neutron absorber in fast breeder reactors is reported. The effect of particle size and sintering temperature on density and microstructure was studied. Pressureless sintering of boron carbide powder (0.5 μm) at 2375 °C yielded a pellet of 93% ρ_{th}. Addition of zirconium dioxide was found to be beneficial in lowering the sintering temperature. A typical sample with 5 wt% zirconia addition sintered at 2275 °C resulted in a density of 93% ρ_{th} and a micro hardness value (HK_{100}) of 32 GPa.

Keywords: A. Sintering; B. Optical microscopy; C. Hardness; E. Nuclear applications; Boron carbide

1. Introduction

Boron carbide is an important non-metallic hard material with high melting point (2450 °C) and hardness. It is generally accepted that in B–C system, one binary phase $B_{13}C_{2\pm x}$ exists with a wide homogeneity range of 8.8–20.0 at.% carbon [1]. Density of boron carbide is 2520 kg/m^3, which increases linearly with carbon content within the homogeneity range. Knoop hardness of pressureless sintered boron carbide and hot pressed material are measured as ~25.5 ± 2.4 GPa and ~29.0 ± 1.5 GPa, respectively [2].

Boron carbide is used as neutron absorber owing to its high boron content, chemical stability and refractory character. Neutron absorption property of boron carbide relies on the presence of B^{10} isotope, which undergoes the main capture reaction:

$$_5B^{10} + {}_0n^1 \rightarrow {}_2He^4 + {}_3Li^7 + 2.4\,MeV$$

Absorption cross section of this reaction is 3850 barns for thermal neutrons, which makes it an excellent candidate for thermal reactors. At higher energies the cross section of most other elements becomes very small, whereas that of B^{10} decreases monotonically with energy [3]. Absolute values in the entire energy spectrum are of sufficient magnitude to make it very effective as neutron absorber in the intermediate and fast energy range. Other industrial uses of boron carbide are as abrasive media for lapping and grinding, polishing media for hard materials and as wear-resistant components.

Due to the presence of high fraction of strong covalent bonding, low plasticity and high resistance to grain boundary sliding, densification of stoichiometric boron carbide (B_4C) is extremely difficult. Simple shapes of dense boron carbide are industrially prepared by hot pressing under vacuum or inert atmosphere fine (<3 μm) pure powder at a high temperature (2100–2200 °C) and pressures of 30–40 MPa for 15–45 min holding time [4]. In case of boron rich carbides, extensive carbon diffusion takes place from the die material towards the sample. Different metallic foils of Ta, Mo and W and boron nitride barrier can be used for protection. Addition of dopants (Mg, Al, B, Fe, Co, Ni, Cu, ZrO_2, TiO_2, etc.) can lower the densification temperature to 1750–1900 °C and hinder grain coarsening [1]. A small addition of boron (1–5 wt%) to the starting boron carbide powder gives pellet with the maximum strength in the temperature range of 1900–2000 °C [5]. High density samples were prepared by hot isostatic pressing (HIP) of boron carbide at a lower temperature (1700 °C). However, the problem exists on the choice of canning material.

* Corresponding author. Tel.: +91 22 25593937; fax: +91 22 25505151.
E-mail address: csubra@apsara.barc.ernet.in (C. Subramanian).

0272-8842/$30.00
doi:10.1016/j.ceramint.2005.02.008

Promising results have been obtained by using a special type of boron oxide glass as the canning material [1]. Pressureless sintered material with 1–3 wt% C addition can be fully densified (>99%) by a post HIP treatment at 2000 °C under argon atmosphere of 200 MPa [6]. In pressureless sintering process, dense pellets could be obtained only with a starting material of fine size in the range of < 3 μm and a sintering temperature of 2250–2350 °C [1]. Kinetics of recrystallization in sintered and hot pressed boron carbide were investigated by Kuzenkova et al. [7]. They found that recrystallization starts at around 1800 °C and grain grows rapidly above 2200 °C. To increase the volume and grain boundary diffusion and thus to cause densification at lower temperatures different additives are used. Densification at 2150–2250 °C can be achieved by adding different inorganic additives such as Si, Al, Mg, SiC, SiC + Al, TiB_2 + C, etc. Recent studies of Levin et al. and Goldstein have shown that the addition of TiO_2 [8] and ZrO_2 [9] to boron carbide powders improves the density values to 95–97% while sintering at around 2200 °C. The addition of carbon in the form of a novolaque type phenol formaldehyde resin (C is 9 wt%) also yields a dense boron carbide pellet (>95% ρ_{th}) [10]. A promising method is the use of two organic precursors, e.g. polycarbosilane with a small amount of phenolic resin [2]. Additives help in the prevention of grain growth and impart better mechanical properties and hardness in the pellets. Recent studies on explosive compaction and subsequent sintering of boron carbide have shown the feasibility of fabricating crack free composites with near theoretical density and high hardness values [11,12].

The present work was aimed at developing a suitable process for the production of dense boron carbide pellets in the density range of 88–93% ρ_{th} for use as neutron shielding in fast breeder reactors. The choice of sintering additives is limited for nuclear application. Though hot pressing method is most suitable for the production of near net shape products, it was not preferred because of its low productivity and high cost. In the above perspective, experimental studies were performed on pressureless sintering of boron carbide. Effects of addition of carbon, titanium boride (TiB_2) and zirconium dioxide (ZrO_2) on the densification were studied. Pellets were characterized by XRD, optical microscopy, SEM, EPMA and microhardness.

Table 1
Chemical analysis of boron carbide and titanium boride

Boron carbide		Titanium boride	
Element	wt%	Element	wt%
B	78.00	Ti	67.21
C	19.05	B	30.25
Fe	1.11	O	0.6
Si	0.45	C	0.5
Ni	0.08	N	0.2
Cr	0.02		
O	0.5		

Table 2
Variation of density with temperature

Serial no.	Particle size (μm)	Temperature (°C)	Density (% ρ_{th})
1	2	2225	80
2		2275	80
3		2325	85
4		2375	87
5	0.8	2300	87
6		2325	88
7		2375	93
8	0.5	2275	81
9		2300	85
10		2375	90

2. Experimental

2.1. Materials

Boron carbide powder used for this study was prepared by carbothermic reduction of boric acid in an Acheson furnace. Chunklets of boron carbide were crushed in a jaw crusher and ground in a hammer mill to obtain particles of less than 45 μm. Fine powders of approximately 1 μm size used in these sintering studies were prepared by micronising these coarse powders in a planetary mill. Impurities picked up during milling were removed by leaching with dilute hydrochloric acid solution. Powders were characterized by chemical analysis and laser particle size analyzer. Fine powders of median diameter of 0.5–2 μm were used in the present investigation. Titanium boride was prepared in the laboratory by the reaction of boron carbide and titanium dioxide in a vacuum induction furnace at a temperature of 1800 °C and a vacuum of 1×10^{-3} Pa. Zirconium oxide used was of reactor grade powder obtained from Nuclear Fuel Complex, Hyderabad. Table 1 presents the chemical analysis of boron carbide and titanium boride.

2.2. Procedure

In case of carbon addition, the calculated amount of phenol formaldehyde resin (1–3% C) was mixed with boron carbide powder and pelletized. These pellets were slowly heated to a temperature of 1000 °C in argon atmosphere to ensure a fine coating of carbon over boron carbide particles. In other cases, ZrO_2 (5 wt%) and TiB_2 (5 wt%) powders were thoroughly mixed with boron carbide powder. Powders were then

Table 3
Variation of density with sintering additives

Serial no.	Sintering additive	Temperature (°C)	Density (% ρ_{th})
1	1 wt% C	2325	91
2	3 wt% C	2325	90
3	5 wt% TiB_2	2375	82
4	5 wt% ZrO_2	2275	93

Boron carbide particle size: 0.5 μm.