Multiphase formation of boron carbide in B_2O_3–Mg–C based micropyretic process

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Abstract

Boron carbide with higher activity of boron is a solution to problems associated with tailoring applications of boron carbide with current B_4C composition. This article elaborates "boron oxide–magnesium–carbon" based micropyretic process for formation of boron rich boron carbides. Influence of change in input phase ratio (B_2O_3:Mg:C), protective argon gas pressure and high compaction load on boron carbide phase formation pattern, have been investigated. Low argon pressure (<1 MPa) along with the stoichiometric ratio (2:6:1) yielded insignificant quantity of boron carbides in the product. The investigation has shown that combination of 620 MPa compaction load, 10.2 MPa argon pressure and phase ratio (2:7.8:1.22) with optimized mineral acid leaching, led to formation of boron rich boron carbide phases. These phases were $B_{13}C_2$, $B_{41.11}C_{4.45}$, B_8C, $B_{50}C_2$, apart from $B_{12}C_3$ and elemental boron. The purity of these boron carbides was more than 99.7%. The average 'boron to carbon' ratio was 5.04. X-ray fluorescence studies, carbon analysis, laser based particle size analysis, X-ray diffraction, XRD peak deconvolution, crystallographic studies and particle morphology studies have been carried out to confirm the overall 'boron to carbon' ratio, structure of multiple boron carbide phases, the submicron size and yield of the process. The resulted crystal structures were rhombohedral, tetragonal and orthogonal. The formation mechanism was observed to be a result of nonlinear characteristics of the micropyretic process. The article also illustrates the possibility of formation of a recently discovered MgB_2C_2 refractory phase under varying optimized condition and its detailed study requires a separate investigation.
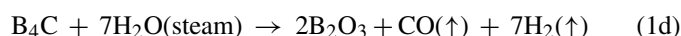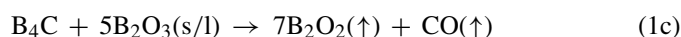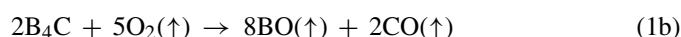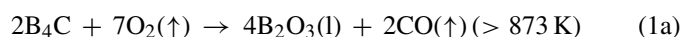© 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Boron carbides are a class of low atomic number ceramic materials. Their noticeable properties are lower specific weight, highest hardness over 1373 K, high modulus of elasticity at high temperature, chemical inertness in extreme environments and the isotopic boron content. Potential engineering applications for boron carbides include refractory liners, dies, bearings, sandblasting nozzles and ballistic protection. For thermal nuclear reactors boron carbide in form of B_4C composition provides a practical approach for controlling neutron fluxes so that the reactor is not self destructive. The neutron absorption efficiency is related to boron content of boron carbide as well as isotopic contents of boron. Boron rich composition will have better neutron absorption efficiency compared to B_4C composition based boron carbide. Literature survey of seventies, eighties and nineties discloses that B_4C is most investigated solid-state formed composition and widely used in commercial boron carbide based products. Such B_4C products loose boron through oxygen contaminants during sintering as well as in high temperature service life by following gross reactions:

$$2B_4C + 7O_2(\uparrow) \rightarrow 4B_2O_3(l) + 2CO(\uparrow)\,(>873\,\text{K}) \quad (1a)$$

$$2B_4C + 5O_2(\uparrow) \rightarrow 8BO(\uparrow) + 2CO(\uparrow) \quad (1b)$$

$$B_4C + 5B_2O_3(s/l) \rightarrow 7B_2O_2(\uparrow) + CO(\uparrow) \quad (1c)$$

$$B_4C + 7H_2O(\text{steam}) \rightarrow 2B_2O_3 + CO(\uparrow) + 7H_2(\uparrow) \quad (1d)$$

The generation of boron suboxides by oxygen contaminants coarsens the microstructure during sintering. The boron loss due to slow in-service oxidation decreases the average boron content and leads to loss of functional properties. Thus, requirement of boron rich boron carbide with varying boron to carbon
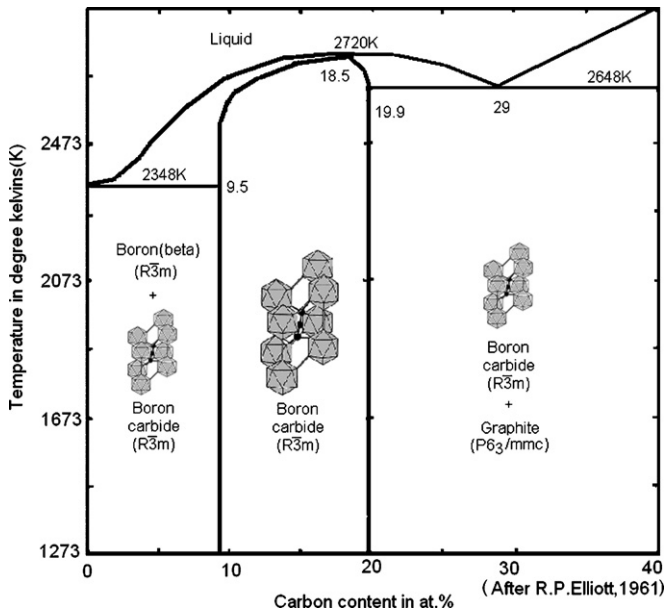

Fig. 1. Phase diagram for the boron–carbon system.

ratio is becoming an emerging issue. Although the variation of physical properties is not fully established, the increase in B/C ratio of boron carbide changes the lattice parameter and which in turn varies structure sensitive physical, chemical and mechanical properties. As observed in Eq. (1a) boroncarbide containing low carbon, will decrease the quantity of carbon species formed during oxidation. However, many useful properties of boron carbide

with varying carbon contents have been discussed by Werheit, Suemastu et al., Niihara et al. and Lezhava et al. [1–4]. For production of boron carbide, many processes have been investigated and these have led to formation of B_4C, i.e., $B_{12}C_3$ composition [5–7]. B_4C composition is formed because of presence of high heat input leading to high temperatures (>2700 K) for long hours. Molten boron carbide wets carbon surface. Thus, in such condition carbon dissolves in as-formed boron to form agglomerated B_4C phase with presence of angular shaped free carbon. Particles of micron size or more and presence of irregular shaped free carbon prevent boroncarbide solids to attain full densification during hot consolidation. So a boron rich boron carbide with submicron size and spherical particles would greatly reduce this disadvantage.

Observation of boron–carbon phase diagram predicts the existence of boron carbide as single rhombohedral phase over an accepted carbon solubility ranging from 8.8 to 20 at.% (Fig. 1). Investigations for compositions other than B_4C are rare except those synthesized in chemical vapour deposition processes [8]. In these processes the formed boron carbides are semi-crystalline in nature and are often contaminated with phases such as $C_2B_{10}H_{12}$ and BN. While such vapour based synthesis is limited to research scale only, B_2O_3–Mg–C based solid-state micropyretic process carried out in thermal explosion mode has a potential for large scale production of non-stoichiometric boron rich boron carbides (Fig. 2). The associated parameters and numerical method of solving problems of micropyretic processes have been studied and established by researcher like Li and Sekhar [9], Li [10,11], Lakshmikantha and Sekhar [12] and
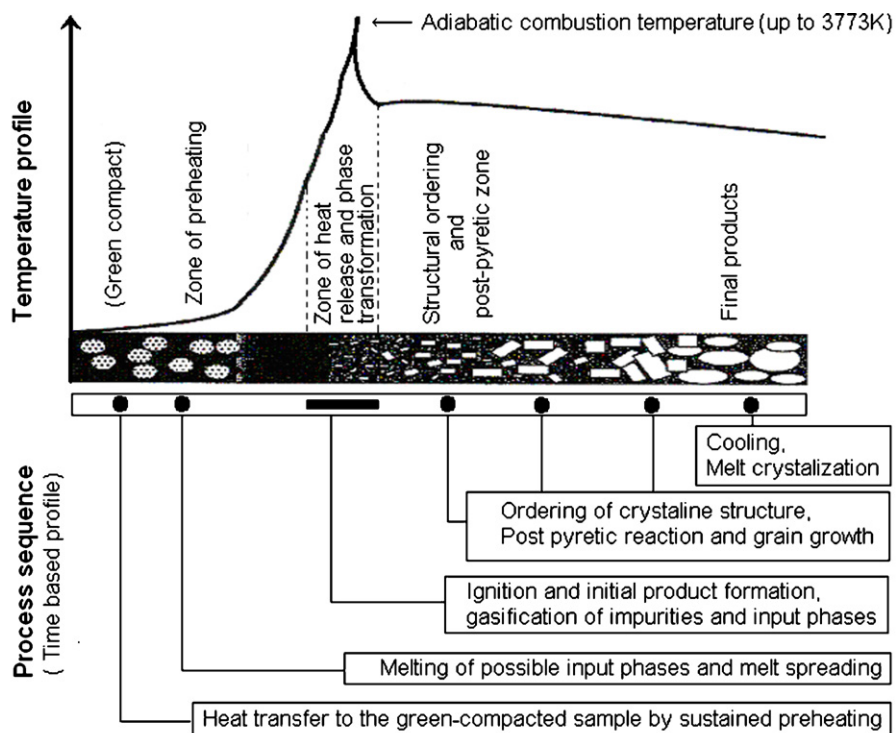
Fig. 2. Temperature profile and process characteristic of a typical micropyretic process (shown through a single heat wave).