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The effect of different sources of porous carbon on the synthesis of nanostructured boron carbide by magnesiothermic reduction

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Abstract

Boron carbide (B_4C) is an advanced engineering ceramic with properties that are improved in highly densified materials. A possible alternative to the use of sintering additives may be the use of nanostructured B_4C powders. This paper reports the synthesis of nanostructured boron carbide by magnesiothermic reduction of boron oxide and porous carbons derived from synthetic ZSM-5 zeolite, mesoporous SBA-15 silicate or mesoporous MCM-48. The syntheses were carried out under argon with different mass ratios of boron oxide, carbon and magnesium. The ZSM-5, SBA-15 and MCM-48 templates and the corresponding porous carbon products were characterized by BET, XRD, TGA, SEM and EDX. The effect of the type and content of the carbon reactant on the boron carbide synthesis suggests that in addition to the type of carbon, the nature of the template is an important factor in the synthesis of nanostructured boron carbide.

Keywords: Boron carbide; Magnesiothermic; Porous carbon; Na-ZSM-5; SBA-15

1. Introduction

Boron carbide is one of the boron-richest solid materials and has a rhombohedral structure [1]. Its hardness is second only to diamond and boron nitride, making it a most promising material for helicopter armor, lightweight armor plates, cutting tools and blasting nozzles [2–4]. Its other useful properties are its low thermal conductivity (30–42 $W\,m^{-1}\,K^{-1}$), high hardness (29–35 GPa), low coefficient of thermal expansion ($5.73\times10^{-6}\,K^{-1}$), high melting point (2450 °C), and good thermal shock resistance [1,2]. Boron carbide was discovered as a by-product of reaction of metal borides [2]. There are several synthesis methods for boron carbide, including carbothermal reaction [5], direct synthesis from boron and carbon [6], deposition from the vapor phase [7], synthesis from polymer precursors [8], sol–gel synthesis [9], VLS growth [10], ion beam synthesis [11] and magnesiothermic synthesis [12]. Some of these synthesis methods suffer from drawbacks; carbothermal synthesis requires high temperatures for long times, the sol-gel method is uneconomic, gas-phase deposition is useful only for thin films and VLS requires a liquid catalyst [2].

On the other hand, exothermic magnesiothermic reduction of boron oxide in the presence of carbon is a convenient method for producing boron carbide of small particle size:

$$2B_2O_3+6Mg+C\rightarrow B_4C+6MgO \quad (1)$$

The reaction occurs in two stages:

$$2B_2O_3+6Mg\rightarrow 4B+6MgO \quad (2)$$

$$4B+C\rightarrow B_4C \quad (3)$$

This reduction synthesis produces fine powders which are very useful to synthesize ceramic bodies. The amount and

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grain size of the reactants, particularly the carbon, influences the reaction temperature and particle size of the nano sized product. Porous materials can be used as templates to produce reactive mesoporous carbons with high surface areas and large massive pores, as shown by Ryoo et al. [13], who used an ordered silicate as the template to synthesize carbon-based molecular sieves by the nanocasting method. In the present study, three ordered materials, a zeolite, the mesoporous silicates SBA-15 and MCM-48 were used as the template of carbon source (sucrose or furfuryl alcohol) and carbonized by heating in argon before removal of the template. The aim of this research was to study the magnesiothermic synthesis of nanostructured B_4C using this series of porous carbons with high specific surface areas.

2. Experimental procedure

The nanostructured boron carbide was synthesized by magnesiothermic reduction of boron oxide using three different nanoporous carbons derived from ZSM-5, mesoporous SBA-15 and MCM-48 as follows:

2.1. Porous carbon synthesis using Na-ZSM-5 as a template.

The chemical composition of the Na-ZSM-5 template, that was prepared according to procedure which explained by nezamzadeh and et al. [14], is shown in Table 1. The zeolite was dehydrated in vacuum at 200 °C, and then impregnated with furfuryl alcohol at room temperature for 72 h at a volume to mass ratio (furfuryl alcohol to NaZSM-50) of 4 cc/g. The excess furfuryl alcohol was removed from the sample by washing with toluene. The resulting solid was polymerized at 150 °C for 8 h then carbonized by heating at 5 °C/min to 900 °C and held at that temperature for 4 h under argon atmosphere. The aluminosilicate template was then removed by leaching at room temperature for 24 h with excess 46% HF, filtered with hot water and dried. This carbon is designated CZSM-5.

2.2. Porous carbon synthesis using SBA-15 as a template

The carbon source (sucrose) was impregnated into the SBA-15 template as follows:

5 ml distilled water, 1.25 g sucrose and 0.14 g 98% sulfuric acid was added to 1 g SBA-15 that was prepared according to procedure which explained by Asgarian and et al. [15] and stirred at room temperature for 15 min until completely homogenized. The mixture was then heated at 100 °C for 6 h, then at 160 °C for a further 6 h. The resulting composite was carbonized in nitrogen at 900 °C and the SBAS-15 template was removed from the black product by refluxing with sodium carbonate solution for 5 h. The solid was then filtered through a Buchner funnel, washed with ethanol and dried. This carbon is designated CMK-3.

Table 1
Chemical analysis (Wt %) of NaZSM-5 zeolite.

SiO_2	Al_2O_3	Na_2O	Fe_2O_3	MnO	TiO_2	CaO	K_2O	SO_3	P_2O_5	MgO	LIO	Total
90.93	2.31	1.65	0.02	0.01	0.02	0.03	0.01	> 0.01	> 0.01	0.04	5.00	100.02