Int. Journal of Refractory Metals and Hard Materials 57 (2016) 31–41

Contents lists available at ScienceDirect

Int. Journal of Refractory Metals and Hard Materials

journal homepage: www.elsevier.com/locate/IJRMHM

# Effect of Al addition on SiC–$B_4C$ cermet prepared by pressureless sintering and spark plasma sintering methods

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ARTICLE INFO

*Article history:*
Received 4 September 2015
Received in revised form 30 December 2015
Accepted 4 February 2016
Available online 23 February 2016

*Keywords:*
Cermet
Powder metallurgy
Sintering
Scanning electron microscopy (SEM)
X-ray diffraction

ABSTRACT

SiC–$B_4C$–Al cermets containing 5, 10 and 20 wt.% of Al were fabricated by high-energy planetary milling followed by conventional sintering and spark plasma sintering (SPS) techniques separately. The average particle size reduced to ~3 μm from an initial size of 45 μm after 10 h of milling. The as-milled powders were conventionally sintered at 1950 °C for 30 min under argon atmosphere and SPS was carried out at 1300 °C for 5 min under 50 MPa applied pressure. The formation of $Al_8B_4C_7$ and $AlB_{12}$ phases during conventional sintering and SPS were confirmed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses. The formation of $Al_8B_4C_7$ at 700 °C and $AlB_{12}$ at 1000 °C was well supported by XRD and differential scanning calorimetry (DSC). The maximum relative density, microhardness and indentation fracture resistance of SiC–$B_4C$–10Al consolidated by SPS are 97%, 23.80 GPa and 3.28 MPa·$m^{1/2}$, respectively.



## 1. Introduction

SiC–$B_4C$ based cermets have drawn considerable attention for research and development in several aero-engine components, cutting tools, heat exchangers, heat engine parts, fusion reactors, armor plates etc. due to their lightweight and high-temperature properties [1,2]. Boron carbide ($B_4C$) and silicon carbide (SiC) have been considered as superior ceramic armor materials because of their low theoretical density, high-temperature resistance and high hardness [1–3]. $B_4C$ has been found to be used with SiC in various applications to control phase transformation, grain growth and to obtain improved mechanical properties [4–9].

Unfortunately, the processing of covalently bonded $B_4C$ and SiC to obtain sufficiently dense products is very difficult [10]. Low plasticity, low diffusion coefficient, and very low fracture toughness limit their applications as structural material [11,12]. To aid sintering, a low melting metallic phase such as aluminum has been added and the effects of Al addition on the microstructure and mechanical properties of SiC–$B_4C$ based cermets have been studied [13]. Ductile Al addition into SiC and $B_4C$ acts as a binder and lowers the sintering temperature. Al metal addition also improves the toughness of the ceramic matrix without impairing the hardness of the carbide phase.

The SiC–$B_4C$ system is densified by solid state sintering at temperatures greater than 2000 °C. High-temperature sintering leads to exaggerated grain growth that is detrimental to the mechanical properties and also un-economical. Omori and Takei [14,15] reported rare earth oxides combined with $Al_2O_3$ and boron could be used to obtain highly dense SiC through liquid phase sintering. $Al_2O_3$, CaO, and $Y_2O_3$ are also added for liquid phase sintering in SiC, where the oxides form a liquid phase at low temperature. These oxides may react with $SiO_2$ present at the surface of SiC to form the liquid phase at low temperature [16–19]. Zhou et al. [20] studied pressureless sintering of α- SiC by adding $Al_4C_3$–$B_4C$–C and observed the addition of these materials to enhance density and toughening. Cho et al. [21] also used Al, B and C additives to enhance densification in SiC. They found that grain growth rate decreases with increase in Al–B–C content in SiC. Williams et al. [22] added Al, B and C to produce dense SiC by pressureless sintering techniques. The addition of Al not only enhances densification but also favours β to α phase transformation of SiC. It imparts high strength and fracture toughness to the matrix. Gilbert et al. [23] used Al, B and C as additives into β-SiC to produce dense SiC by hot pressing. Cao et al. [24] also found similar observations made by Williams et al. [22]. Mashhadi et al. [25] studied the effect of Al addition on pressureless sintering of $B_4C$ and found that density and grain size depend on the Al amount.

Spark plasma sintering (SPS) is an advanced sintering technique that densifies materials at much lower temperature, especially promising for those materials that are difficult to sinter by conventional sintering methods. Advantages of SPS over conventional pressureless sintering include faster heating rates, shorter dwell time that retain finer microstructure, and imposition of DC pulsed current that enhances mass transport by electro migration [26–29]. There is elimination of adsorptive gas and impurities existing on the surface of powder particles by

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http://dx.doi.org/10.1016/j.ijrmhm.2016.02.005
0263-4368/

localized high-temperature spark impacts. The high-speed ion migration between contacting particles possibly due to the applied electric field is mainly responsible for promoting sintering by enhancing diffusion and thereby material transfer in micro and nano levels [30]. On the contrary, conventional sintering process is carried out at higher temperature with prolonged time, resulting in grain growth and concomitant inferior mechanical properties.

Although there are several reports on the fabrication of SiC–$B_4C$ ceramics by pressure assisted sintering technique, limited work has been carried out on the addition of a metal (namely Al) into SiC–$B_4C$ during pressureless sintering. Moreover, there are no reports available on the synthesis of SiC–$B_4C$–Al cermets by spark plasma sintering (SPS). Hence, the present study attempts to prepare SiC–$B_4C$–Al cermets by both pressureless sintering and SPS and study the effect of Al addition on their microstructures and mechanical properties. Finally, a comparative study has also been carried out on the synthesis of SiC–$B_4C$–Al cermet between these two techniques.

## 2. Experimental

The SiC–$B_4C$–Al cermets were fabricated using Analar grade raw elemental powders of SiC, $B_4C$, and Al (purity > 99% and initial average particle size < 45 μm). The powders were blended to make the nominal compositions 60SiC35$B_4$C5Al, 60SiC30$B_4$C10Al and 60SiC20$B_4$C20Al (all in wt.%). These compositions were milled in a Fritsch planetary (P5) mill at a speed of 300 rpm for 10 h. Chrome steel balls of diameter 10 mm were used and the ball to powder weight ratio of 6:1 was maintained and milling was carried out in toluene to prevent oxidation. The milled powders were collected at intervals of 0, 2, 5 and 10 h of milling. The phase, surface morphology and particle size distribution of the milled powders were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and particle size analyzer (Malvern, Mastersizer), respectively. For the size distribution studies, milled powders were dispersed into a solution of 500 ml distilled water and 25 ml of sodium hexametaphosphate (1 l distilled water + 2 g of sodium hexametaphosphate powder). Thermal analysis of the milled powders was carried out by differential scanning calorimetry (Netzsch, Germany) during which the samples were heated from room temperature to 1200 °C at a heating rate of 10 °C/min under argon atmosphere.

The as-milled powders were compacted into pellets in a hydraulic press followed by conventional sintering in a tubular furnace at 1950 °C for 30 min in argon atmosphere.

In another set of experiments, the as milled powders were loaded into a graphite die and SPS (Dr. Sinter, SCM 1050, Japan) was carried out at 1300 °C with a heating rate of 100 °C/min and held for 5 min under 50 MPa pressure.

After sintering, the bulk density was measured by the Archimedes' method. The phases developed in the milled powders and sintered pellets were analyzed by Rigaku Japan model: Ultima IV multipurpose X-ray diffraction system using Cu-$K_\alpha$ ($\lambda = 1.54$ Å) radiation. The morphology and phase distribution were studied by an optical microscopy to which an Axio-vision software was attached. For structural and morphological analysis, JEOL JSM-6480 LV scanning electron microscopy (SEM) and field emission scanning electron microscopy (FESEM) of NOVA NANOSEM 450 were used. The sintered samples were mirror polished with diamond paste for microstructural analysis. The microstructure was revealed by chemically etching the samples with Murakami reagent that attacks the grain boundary phases [6]. Murakami etchant was prepared by mixing 10 g $KNO_3$ and 10 g $K_3Fe(CN)_6$ into a solution of 100 ml distilled water and10 ml $HNO_3$. Microhardness of sintered samples was measured by Vickers microhardness tester (Leco Microhardness tester LM248AT) at an indentation load of 2.94 N for a dwell time of 10 s. Indentation fracture resistance of sintered samples was calculated by Vickers indentation method at an indentation load of 98 N, in which Niihara equation was used for calculation.

## 3. Results and discussion

### 3.1. Morphology of as received powder

Fig. 1 shows the SEM micrographs that reveal the size, shape and morphology of as received SiC, $B_4C$, and Al powders. From the figure, it has been observed that SiC and $B_4C$ powder particles are irregular in shape with sharp edges, whereas Al powders are dendritic in nature. SEM analysis confirms the as received powder size of SiC, $B_4C$, and Al to be in the range of 25–45 μm.

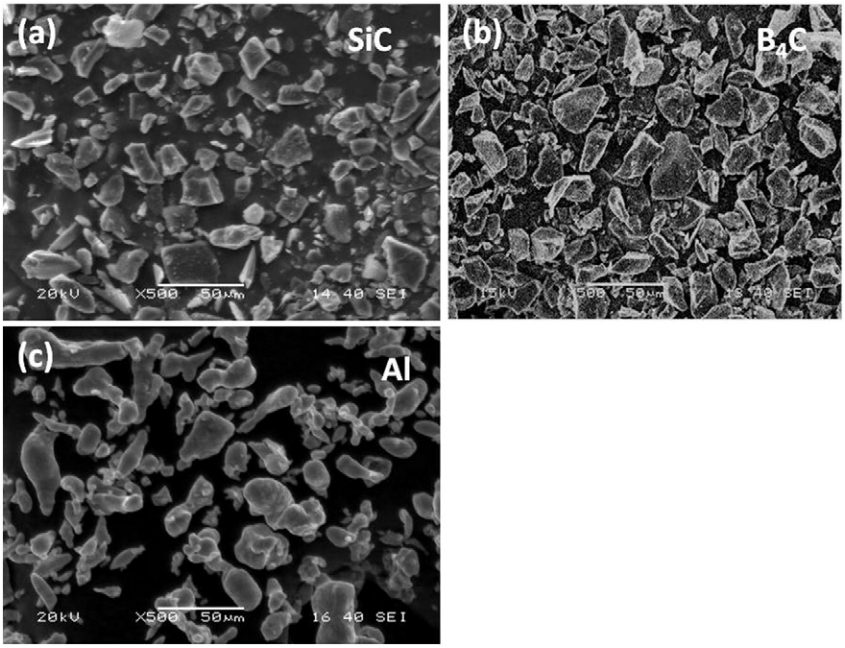


**Fig. 1.** SEM micrographs of as received powders: (a) SiC, (b) $B_4C$ and (c) Al respectively.