

Deposition of a Ni₃P nano-scale layer on B₄C nanoparticles by simple electroless plating in an acidic bath

Mohsen Hajizamani · Ali Alizadeh ·
Naser Ehsani

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Abstract In this study, deposition of a Ni₃P nano-scale layer on B₄C nanoparticles via simple electroless plating in an acidic bath was investigated. B₄C nanoparticles were produced by mechanical milling with the average size of about 95 nm. Electroless nickel plating was carried out at temperature and pH of 85°C and 5.5, respectively. The uncoated and composite powders were characterized by transition electron microscope and the phases present were revealed by X-ray diffraction. Also, nickel and phosphorous contents of the coating were measured by inductively coupled plasma analysis. The results confirmed deposition of a Ni₃P layer with the average thickness of about 25 nm on B₄C nanoparticles.

Keywords Electroless plating · B₄C nanoparticles · Ni₃P nano-scale layer · Acidic bath · TEM

Introduction

Ceramic particles like B₄C, Al₂O₃, SiC and MgO in nanometric scale have absorbed attractions to be used as reinforcements since they reduce interparticle spacing resulting in increased mechanical properties (Ansary Yar et al. 2009).

Various mechanical methods like high energy processes such as planetary, attrition and jet milling are available to prepare ultra fine particles (Aparecida et al. 2006). Attrition mill has been widely used for fine grinding of different materials. The main advantages of attrition mills are

relatively high energy utilization, fast and efficient fine grinding and simple operation (Shinohara et al. 1999).

Boron carbide has a low density, high hardness and offers distinct advantages such as neutron absorption, wear resistance and impact resistance (Lee et al. 2001). These unique properties make B₄C a proper candidate to fabricate MMCs especially Al matrix composites. One of the major problems to do this is poor wettability of ceramic particles like B₄C with the matrix (Kerti and Toptan 2008). To overcome this problem, there are several ways including: (i) adding surface-active elements into the matrix; (ii) increasing metal liquid temperature; (iii) oxidizing or coating the ceramic particles; (iv) using inert or reactive gases during production; and (v) changing the chemical composition of the matrix alloy (Hashim et al. 2001; Tekmen and Cocen 2006; Tekmen et al. 2007). Therefore, one of the most important procedures to enhance wettability is deposition of a metallic or alloy coating on ceramic particles. One way to do this is through electroless plating of metals on ceramic particles. Electroless plating has been used in preparation of low dimensional nanostructured materials. Some results have been reported to deposit metals or metallic compounds on the surface of carbon nanotubes, nano and micron particles of SiC, and Al₂O₃ powders, etc. (Kong et al. 2002; Chen et al. 2003; Chang and Lin 1996; Zhang et al. 2003).

The reduction of nickel during electroless plating is a simple reaction. It is clear that electroless nickel plating consists of autocatalytic deposition of Ni–P alloy from an aqueous solution with no usage of external current (Abrantes and Correia 1994; Ashassi-Sorkhabi and Rafizadeh 2004). The characteristics of the alloy coating expand the physical properties beyond those of pure nickel coating. These unique properties include corrosion and wear resistance (Sankara Narayanan and Seshadri 2004), hardness, lubricity,

M. Hajizamani · A. Alizadeh (✉) · N. Ehsani
Faculty of Materials and Manufacturing Processes, MUT,
PO Box 15875-1774, Tehran, Iran
e-mail: al.alizad53@gmail.com

uniformity of deposit regardless of geometries and non-magnetic properties (Ramalho and Miranda 2005).

The major novelty of the present study is that there are few reports on deposition of a metallic or compound coating on the nano-scale ceramic particles and no reports on formation of such a coating on micron or nano-scale B_4C particles. Due to agglomeration of nanoparticles, deposition of a coating layer on these particles is very difficult. On the other hand, the product of this study can be considered as a nanocomposite powder which can be used as modern nano-scale reinforcement in fabrication of MMCs especially Al matrix composites with better wettability of the ceramic reinforcement with the metallic matrix. In this study, deposition of a Ni_3P nano-scale layer on B_4C nanoparticles via simple electroless in an acidic bath was carried out.

Experimental

B_4C nanoparticles were synthesized by milling of original B_4C powders with the mean size of 0.8 μm in an attrition mill (union process, model 1-S) using a hardened stainless steel vial and hardened stainless steel balls with 6 mm in diameter. The ball to powder ratio and rotational speed were 15:1 and 400 rpm, respectively. Isopropyl alcohol was used as milling media and the grinding media occupied 80% of the chamber volume. The final mean size of the attrition-milled particles was about 95 nm after 140 h milling.

The process of electroless plating consists of two stages: pretreatment of B_4C nanopowder and electroless plating.

Pretreatment of boron carbide nanopowder

The pretreatment of B_4C particles was carried out according to the following procedure:

1. Cleaning by immersing in 150 ml acetone with ultrasonication for 15 min.
2. Cleaning and etching in 150 ml HNO_3 with ultrasonication for further 15 min.
3. Sensitization in a solution containing 10 g/l of $SnCl_2$ and 40 ml/l HCl for 20 min.
4. Activation in a solution of 0.25 g/l of $PdCl_2$ and 2.5 ml/l of HCl for 20 min.
5. Drying at 100°C.

Between the above mentioned stages, complete rinsing was required to prevent contamination of solutions.

Electroless plating

Electroless plating of nickel was performed by introducing about 0.5 g of the pretreated B_4C nanopowder into an

Table 1 Electroless bath composition

Component	Concentration (g/l)
Nickel chloride	45
Sodium hypophosphite	15
Sodium citrate	100
Ammonium chloride	50

electroless plating bath using composition given in Table 1. To expose all of the particles to the electroless nickel solution, continuous stirring was done at 200 rpm. The bath operation started under acidic conditions; the particles were plated at 85°C. Since this temperature has been used as bath temperature in some previous studies (Palaniappa et al. 2007; Kretz et al. 2004; Pai and Rohatgi 1975; Tekmen and Cocen 2008; Zhang et al. 2007a, b) we selected 85°C as the plating temperature. It has been reported that the higher the plating temperature, the more the rate of plating and deposited layer but the temperatures higher than 90°C may lead to bath instability and fail to deposit a coating layer on the particles (Krishnan et al. 2006).

The bath pH measured to be 5.5 and the plating time was 25 min.

The as-received and Ni_3P -deposited B_4C powders were characterized by X-ray diffraction (Siemens X-ray diffractometer, 30 kV and 25 A), scanning electron microscope (SEM-Philips XL 30) and transition electron microscope (TEM- Hitachi H 800). Also, to determine the composition of the coating layer, inductively coupled plasma analysis (Liberty-RL ICP Varian) was carried out. In order to obtain a more trustable data, the analysis was repeated two more times and the average value was presented in the article.

Results and discussion

Morphology and particle size distribution of B_4C nanoparticles

As-received B_4C powder with the mean particle size of about 0.8 micron was used as the starting material. SEM micrographs of as-received powder reveal that the powder has a wide size distribution and irregular shape Fig. 1a.

Figure 1b shows the variation of particle size distribution and median size (D_{50}) as a function of milling time measured by particle size analyzer. By increasing the milling times, decrease in particle size and a narrow sized distribution can be seen.

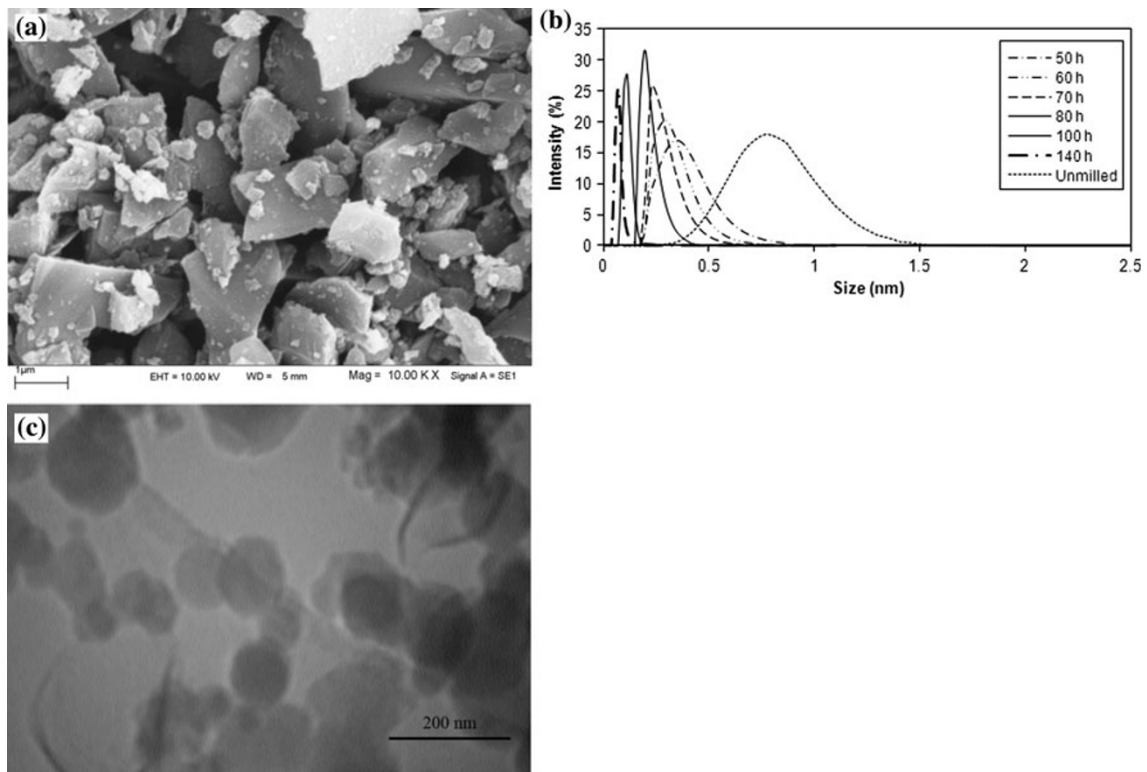


Fig. 1 **a** SEM micrographs of the as-received B_4C particles, **b** particle size distribution of the ball milled boron carbide, **c** TEM micrograph of B_4C particles after 140 h milling

Fig. 2 XRD pattern of **a** attrition-milled B_4C **b** deposited- Ni_3P powder as the product of electroless plating

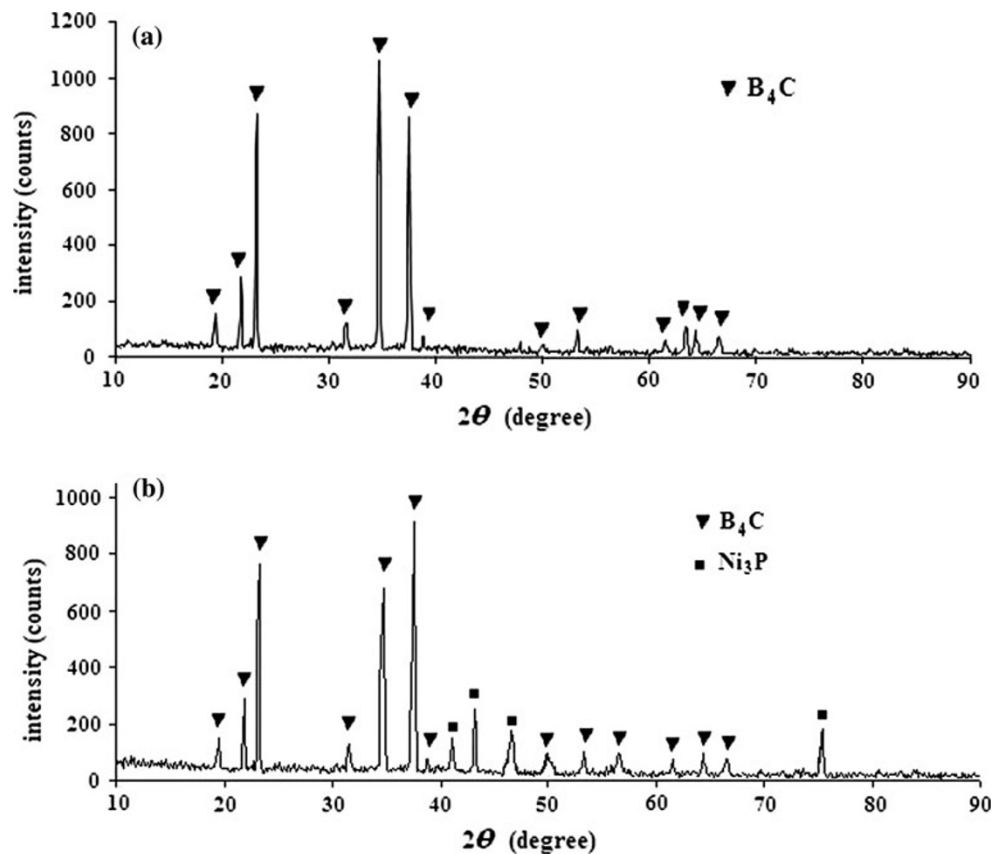


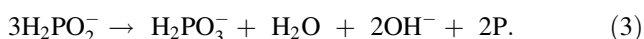
Table 2 ICP analysis results

Element	Weight percentage
Nickel	4.64
Phosphorous	0.92

During milling, a combination of fracture mechanisms occurs which include abrasion, compression and impact mechanism. The particle size distribution of a material after grinding will be determined by the combination of all mechanisms. The predominant mechanism is determined according to material properties and operating conditions. Since hard materials are difficult to be abraded on their surfaces, the impact mechanism plays the dominant role, thus, the distribution curve shows a monomodal distribution curve. This result is consistent with that reported regarding grinding of diamond by a researcher (Shinohara et al. 1999). Figure 1c presents the TEM image of the nanoparticles. The nanoparticles are spherical and have a uniform distribution. The XRD pattern, shown in Fig. 2 a, reveals that the attrition-milled nanopowder consists B₄C phase with no major impurities.

Ni₃P-deposited powder

The mechanism of reduction of nickel ion by hypophosphite has been under constant revision in recent years. The following partial equations occur during electroless nickel plating process in a hypophosphite bath according to the reports of a study (Krishnan et al. 2006):



Therefore, nickel and phosphorous are reduced in the bath simultaneously. The reduced nickel reacts with the reduced phosphorous in the following reaction:



According to reaction (4), an alloy layer of nickel and phosphorous is formed on the particles. This is confirmed by the XRD pattern of the electroless-coated powder in Fig. 2b. The XRD patterns of attrition-milled B₄C powder and coated powder are shown in Fig. 2. In Fig. 2a, only diffraction peaks of B₄C can be observed but in Fig 2b, peaks of Ni₃P can be seen in addition to B₄C peaks.

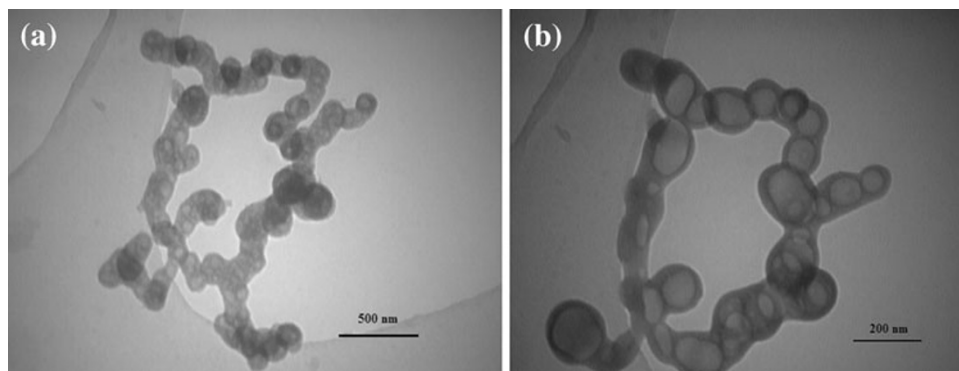
Although in some studies (Krishnan et al. 2006, Ebrahimi-Hosseini et al. 2006), it has been reported that the coating deposited through electroless plating is amorphous and the associated XRD peaks turn up only after heat treatment of the product at 400°C for 1 h, but it should be mentioned that according to results reported by a research (Vafaei-Makhsos et al. 1978), electroless coatings containing up to 5 wt. % phosphorous are crystalline. Thus, phosphorous content of the coating determines the structure of the deposited coating. Table 2 shows the results of ICP analysis which confirms that the phosphorous content of the deposited layer in the present study is below 5 wt. %.

The transition electron microscope images of the as-received and Ni₃P-deposited powders prove deposition of a coating on B₄C nanoparticles. It is clear that the particles are sphere-like. Figure 3 reveals the Ni₃P-deposited nanoparticles by electroless nickel plating with two different magnifications. From Fig. 3b, the average thickness of the nickel phosphide coating layer can be estimated as 25 nm. However, because of high chemical activity of nanoparticles (Zhang et al. 2007a, b), agglomerates of the powder have been formed.

Conclusion

Deposition of a Ni₃P nano-scale layer on B₄C nanoparticles via simple electroless plating was performed at 85°C, pH 5.5, plating time of 25 min and sodium hypophosphite content of 15 g/l. B₄C nanoparticles were produced by mechanical milling. ICP analysis of Ni₃P-deposited particles showed the existence of nickel and phosphorous and the

Fig. 3 TEM images of fabricated Ni₃P-deposited powder with two magnifications



XRD pattern of the product confirmed the presence of these two elements in the coating in the form of Ni_3P . TEM images of the product confirmed this conclusion by showing a coating layer of about 25 nm in thickness.

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