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Electroless nickel–phosphorus coating on boron carbide particles

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ABSTRACT

The present work aimed at studying electroless coating of nickel–phosphorus (Ni–P) onto boron carbide (B_4C) particles with average particle sizes of 93 and 32 μm. Prior to the coating process, B_4C particle surfaces were sensitized using $SnCl_2$ and HCl solution and activated in $PdCl_2$ and HCl solutions. In the electroless coating bath, nickel sulphate ($NiSO_4 \cdot 6H_2O$), sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$) and sodium citrate ($Na_3C_6H_5O_7.5, 5H_2O$) were used as Ni^{2+} source, reducing agent and complexing agent, respectively. The morphology and the chemical composition of the coating layers were characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Characterization results showed that B_4C particle surfaces were successfully coated by a homogeneous and continuous Ni–P layer.

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1. Introduction

B_4C is one of the super-hard materials with its hardness (2900–3900 kg/mm^2) just below that of diamond [1,2]. Furthermore B_4C has excellent wear and chemical resistance, high melting point (2350 °C), low density (2.52 g/cm^3) and very high neutron absorption cross-section, make it extremely suitable for both room and high temperature applications. Therefore, B_4C has been used for lightweight ceramic armour, wear-resistant components such as blasting nozzles and grinding wheels, and control rods in nuclear reactors [3–5]. In addition to the many applications, particulate B_4C is used as reinforcement for composite materials in order to increase physical and chemical properties [6]. However, there are some limitations due to the poor wetting behaviour of B_4C particles. Wettability can be improved by coating of B_4C particles [7]. It has been reported that ceramic–metal contact could be improved by a nickel layer on the ceramic particles [8].

Electroless coating has been considered as a very promising technique to provide a metallic layer on B_4C particle surfaces [9]. This technique is a chemical reduction process, which is based on the catalytic reduction of a metallic ion in an aqueous solution containing a reducing agent and the subsequent deposition of the metal without using electrical energy [10]. Electroless nickel coating is widely used for its high physical, mechanical, tribological and chemical properties [11]. These processes are grouped as Ni–P, Ni–B and pure Ni, based on the reducing agents used (i.e., hypophosphite, borohydride or dialkyl amino borane and hydrazine, respectively) in the coating baths [12]. Hypophosphite is one of the strongest reducing agents for electroless Ni–P coating process which is much cheaper than electroless Ni–B coatings [10,11]. Electroless nickel coating process offers unique deposit properties including uniformity of coating thickness, therefore, it is applied on micro and nanosized particles (carbides, borides, nitrides, oxides, diamond and graphite etc.) to improve their specific properties [10,13]. Lu et al. coated different thicknesses of Ni–B nanolayers on B_4C particles and reported that, when targeted Ni–B nanolayer thickness is $\geq$5 nm, the coating layer is continuous and completely covers the B_4C particle surfaces [9]. Chen et al. coated Ni–P successfully on the surface of silicon carbide nanoparticles [14]. The authors stated that pre-treatments of the silicon carbide nanoparticles are necessary before the electroless plating of nickel. Vaghefi et al. indicated that Ni–P–B_4C composite coatings can be achieved in a conventional electroless nickel phosphorus bath with a suitable suspension of B_4C particles [3]. However, to the best of our knowledge, electroless Ni–P coatings on B_4C particles have not been studied yet. The present paper investigates electroless Ni–P coatings on different sizes of B_4C particles.

2. Experimental procedure

2.1. Materials

B_4C particles with average particle sizes of 93 and 32 μm (with 0.176 and 0.253 m^2/g specific surface areas, respectively) were used in this study. B_4C particle surfaces were sensitized by $SnCl_2$ and HCl solutions (Merck, Germany) and activated by $PdCl_2$ and HCl solutions (Merck, Germany). Nickel sulphate ($NiSO_4 \cdot 6H_2O$, Merck, Germany) was used as the Ni^{2+} source and tri-sodium citrate ($Na_3C_6H_5O_7 \cdot 5, 5H_2O$, Merck, Germany) was used as a complexing agent during deposition process. Sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$, Merck, Germany) was used as a reducing agent, which is also a source of phosphorous in the

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Table 1
Chemical compositions of electroless Ni–P coating bath.

Solution	Concentration
Sensitization bath	
$SnCl_2 \cdot 2H_2O$	12 g/L
HCl	40 ml/L
Activation bath	
$PdCl_2$	0.2 g/L
HCl	2.5 ml/L
Electroless Ni–P coating bath	
$NiSO_4 \cdot 6H_2O$	55 g/L
$NaH_2PO_2 \cdot H_2O$	20 g/L
$Na_3C_6H_5O_7.5, 5H_2O$	122 g/L

electroless coating bath. Ammonia solution (Merck, Germany) was used to adjust the pH.

2.2. Pre-treatment of B_4C particle surfaces

The electroless coating process consists of three basic operations: sensitisation, activation and coating. Prior to the coating process, B_4C particle surfaces were sensitized in 12 g/L $SnCl_2 \cdot 2H_2O$ and 40 ml/L HCl solutions for 15 min at room temperature followed by the activation of B_4C particle surfaces in 0.2 g/L $PdCl_2$ and 2.5 ml/L HCl solutions for 15 min at room temperature [15].

2.3. Coating of B_4C particles

After sensitization and activation operations, B_4C particles were introduced into the electroless coating bath containing nickel sulphate as the Ni^{2+} source and sodium hypophosphite as the reducing agent. Free Ni^{2+} ions cause formation of $Ni(OH)_2$ under alkali conditions in aqueous solution. In order to prevent formation of $Ni(OH)_2$, Ni^{2+} ions must be complexed with a stronger complexing agent than water [2]. The complexing agents used for coordinating nickel ion alkaline coating baths are generally combinations of citrate and ammonium ions [16]. In the present study, sodium citrate was used as a complexing agent. Ni/B_4C ratio was adjusted to obtain 750 nm coating thickness. Table 1 gives the composition of solutions used during the electroless coating process [15]. The bath pH was kept between 8 and 9 with ammonia solution, the bath temperature was kept constant at 80 ± 2 °C and the bath stirred by a magnetic stirrer during the coating process.

2.4. Characterization

The surface morphology of electroless Ni–P coated B_4C particles were investigated by SEM, (JEOL JSM-5410), and the composition of electroless Ni–P coated B_4C particles were analysed by EDS.

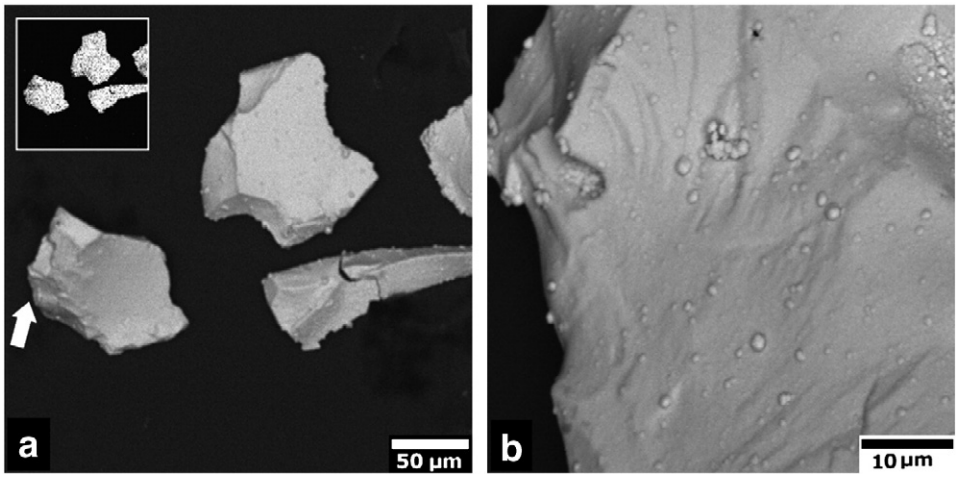


Fig. 1. a) SEM image of Ni–P coated B_4C particles with an average particle size of 93 µm and Ni X-ray map (upper left); b) detailed view of the marked region.

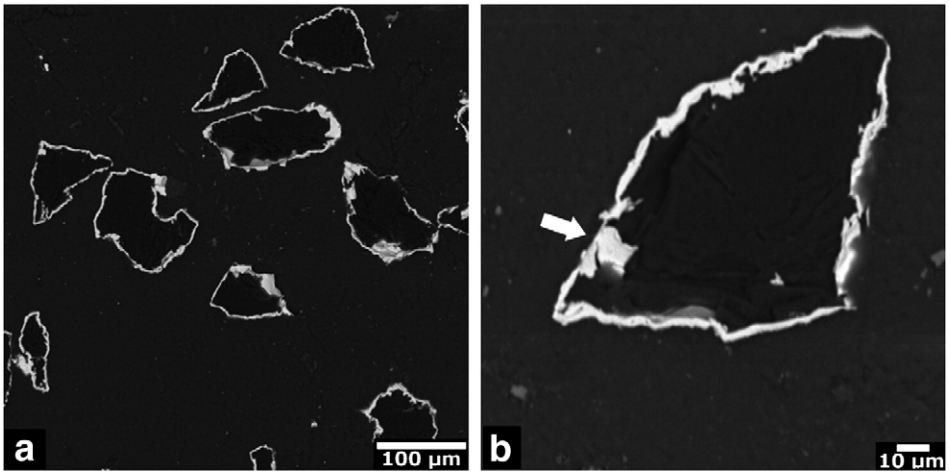


Fig. 2. a) Low and b) high magnification SEM cross-section images of the coated B_4C particles with an average particle size of 93 µm.

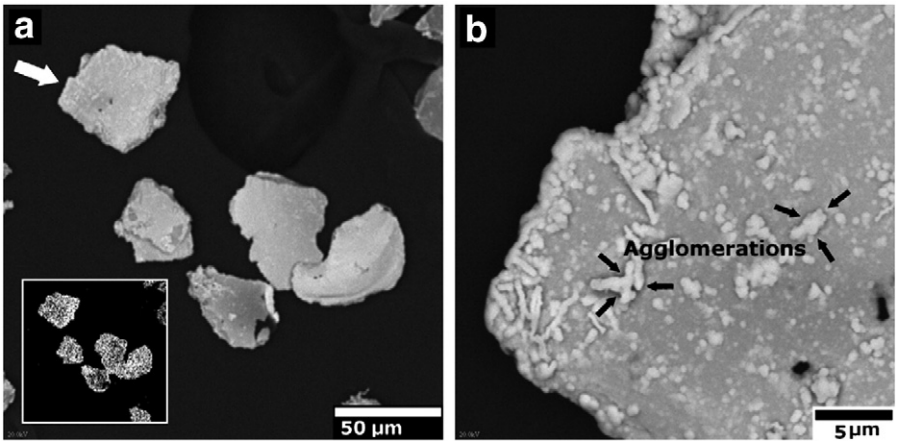


Fig. 3. a) SEM image of Ni–P coated B_4C particles with an average particle size of 32 µm and Ni X-ray map (bottom left); b) detailed view of the marked region.

3. Results and discussion

Fig. 1 shows the SEM images of Ni–P coated B_4C particles with an average particle size of 93 µm. As can be seen on the micrographs, B_4C particle surfaces were successfully coated with a continuous Ni–P layer. Fig. 1b shows the higher magnification image of the coated surface. It was observed from the detailed images that the coating layer completely covers the B_4C surfaces.

The coated particles were mounted into a polymeric resin and polished in order to observe the thickness and the continuity of the coating layer. Fig. 2. exhibits the SEM cross-section images of Ni–P coated B_4C particles with an average particulate size of 93 µm. The cross-section images show that the coating layer continuously surrounds the B_4C particles with a reasonably homogenous thickness.

Fig. 1. shows the SEM images of Ni–P coated B_4C particles with an average particle size of 32 µm. Similar to the coarse B_4C particles, fine particles were also successfully coated with a continuous Ni–P layer. However, unlike the coarse particles, some agglomerations were observed on the coated fine particle surfaces that could not be removed during the cleaning process (Fig. 3b).

Fig. 4. shows the SEM cross-section images of Ni–P coated B_4C particles with an average particulate size of 32 µm. The thickness of the coating layer is approximately 1700 nm in Ni–P coated coarse particles (Fig. 2b) and approximately 1200 nm in Ni–P coated fine particles (Fig. 4b). The targeted Ni–P thickness was 750 nm for both particle sizes of B_4C powders. However, the actual thickness is higher than the targeted thickness values for both particle sizes. The main factors that might have contributed to this discrepancy are:

i) The Ni–P layer is softer than the extremely high B_4C particles. During the polishing, the coating layer deforms and sometime "smears" over the B_4C particle surfaces (Fig. 2b). Therefore, the coating layer can be seen thicker than the targeted values.
ii) The Ni–P coating layer cross-section may not be representative for the smallest layer thickness orientation; a tilt direction can give thicker coating layers around the particles [9].

Zhu et al. [9] studied coating of different thicknesses of nickel–boron nanolayers onto boron carbide particles and reported that, when the targeted Ni–B thickness was 5 nm, the cross-section thickness was 43 nm and when the targeted Ni–B thickness was 50 nm, the actual nanolayer cross-section thickness was 90 nm. In addition to the reasons given above, the authors also reported that, the targeted nanolayer thickness was based on pure nickel content calculation. However, nickel oxidizes during the electroless coating and boron is incorporated into the coating in B_2O_3 format and these oxides increase the Ni–B coating thickness.

4. Conclusions

From this study, the following conclusions can be drawn:

- Electroless coating in sodium hypophosphite bath gives uniform and continuous Ni–P layers on B_4C particles with average particle sizes of 93 and 32 µm.

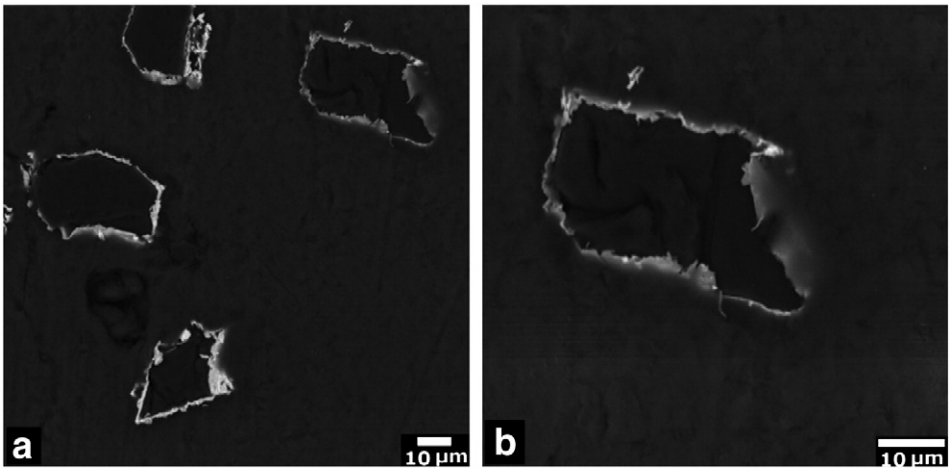


Fig. 4. SEM cross-section images of Ni–P coated B_4C with an average particulate size of 32 µm at (a) low magnification, and (b) high magnification.

- The electroless nickel coating of the coarse particles resulted in better surface quality as compared to the fine particles.

Acknowledgments

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