Sezen G, Kilicarslan A, Daglılar S and Kerti I (2016) Autocatalytic Ni-P and Ni-B deposition on SiC powders. *Emerging Materials Research* **5(1)**: 147–152, http://dx.doi.org/10.1680/jemmr.15.00034

Emerging Materials Research
Volume 5 Issue EMR1
Themed issue: TMS 2015 – Recent developments in biological, structural and functional thin films and coatings
Received 08/05/2015 Accepted 18/04/2016
Keywords: coatings/morphology/surface

ice | science

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Autocatalytic Ni-P and Ni-B deposition on SiC powders

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Ceramic particles such as silicon carbide (SiC) have attracted great attention because of their usability as reinforcement for composite materials. Autocatalytic (electroless) nickel deposition is an excellent process for the enhancement of surface properties of ceramic particles. In this study, deposition of nickel–phosphorus (Ni-P) and nickel–boron (Ni-B) layer on SiC particles by way of autocatalytic plating in hypophosphite and borohydride baths was investigated. SiC powders were sensitised and activated respectively in order to ensure catalytic properties. Electroless nickel coating was performed from two different nickel ion sources (nickel chloride, nickel sulfate) following the pretreatments of particle surfaces. Coated powder morphologies were characterised by scanning electron microscopy. Energy-dispersive spectroscopy analysis was used to investigate the chemical analysis of coatings. The results showed that a better uniformity and bonding were obtained for Ni-P coatings with the Ni^{2+} source of $NiSO_4.6H_2O$ as compared to $NiCl_2.6H_2O$. For Ni-B coatings, the Ni^{2+} source of $NiCl_2.6H_2O$ has provided better quality and continuous coating layer on SiC surfaces.

1. Introduction

Silicon carbide (SiC) ceramic powders have remarkable strengths, such as superior hardness, wear resistance and corrosion resistance, which make them ideal reinforcing materials in metal matrix composites (MMCs), such as Fe-, Al- and Mg-based materials.[1,2] Although SiC powders are covalently bonded ceramics with very stable chemical properties, chemical reactions that easily occur on SiC metal surfaces during the preparation of SiC powders/metal composite materials (such as aluminum, iron, titanium and magnesium) can worsen the performance of the composite materials.[3] Among the solid particles used for reinforcement, SiC is most frequently studied and applied. The thermal, mechanical and chemical properties of SiC make it a promising candidate material for future aerospace and nuclear applications.[4–6] SiC particle is also mostly used among the solid particles for reinforcement to produce MMCs.[7,8] Unfortunately, poor wettability between ceramic reinforcement particles and molten metal for MMC production by casting is still a big challenge.[9,10] Recently, the surface modification of ceramic particles has been studied widely using various methods, including chemical vapor–liquid reaction,[11] atomic layer deposition,[12–14] spray drying,[15] hydrothermal route,[16] seed-mediated growth technique[17] and electroless plating.[18,19] Such properties include magnetic, electrical and chemical properties, as well as the wetting property between metals and ceramic materials. Among metal-coating methods, electroless plating has been recognised as one of the most effective techniques.[20]

Metal-coated ceramic particles are composite powders with a ceramic core and metallic shell. These particles are more suitable for electrical, magnetic and chemical properties and have improved wettability compared to non-coated particles. Poor binding between molten metal and non-coated ceramic particles is a consequence of their low wetting behavior. Metallic coatings of nickel or copper are used to improve the wettability of reinforcement within the matrix material and thereby cause a good bond between matrix alloy and reinforcement.[21] Among the above techniques, electroless plating is considered to be more effective due to its low cost, easy-to-control procedure and large-scale production abilities. The nickel coatings produced by the electroless nickel (EN) deposition have already achieved remarkable results in the area of modifying the SiC surface against interfacial reaction and weak wettability in MMCs.[1,22]

EN coating has been widely studied because of its attractive properties such as good ductility, lubricity and excellent electrical properties.[23] 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.[24] 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.[25] Hypophosphite is one of the strongest reducing agents for the electroless Ni-P coating process, which is much cheaper than

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electroless Ni-B coatings.[25,26] Even though hypophosphate has been widely studied as a reducing agent, inclusion of phosphorus in the nickel coating is not very attractive; boron-containing reducing agent is much preferred. Sodium borohydride ($NaBH_4$) is one of the most powerful reducing agents for electroless Ni-B coating.[27]

In this study, the intent is to coat SiC particles with different nickel ion source Ni-B and Ni-P nanolayers using the electroless coating process and study the layer morphology and forming mechanism.

2. Experimental

2.1 Pretreatment of powders

Figure 1 shows the flow chart of the Ni coating procedure. The SiC powders were pretreated in two steps after washing in acetone for 20 min to remove impurities on the surfaces using ultrasonic bath followed by drying, and SiC particles were sensitised using $SnCl_2$ at room temperature for 15 min and activated using $PdCl_2$ at same conditions with sensitisation. After the pretreatment steps, the powders were cleaned with deionised water and then dried in the oven at 105°C.

2.2 Coating procedure

After pretreatment operations, SiC particles were transferred into the electroless coating bath containing nickel sulfate ($NiSO_4.6H_2O$) or nickel chloride ($NiCl_2.6H_2O$) as the Ni^{2+} source and sodium hypophosphite (NaH_2PO_2) as the reducing agent. The complexing agent was used for coordinating nickel ion in alkaline coating baths. Sodium citrate ($Na_3C_6H_5O_7$) was used as a complexing agent. The bath pH was kept between 8 and 9 with ammonia solution (NH_3(aq)), and the bath temperature was kept constant at 80 ± 2°C. The bath was stirred by a magnetic stirrer

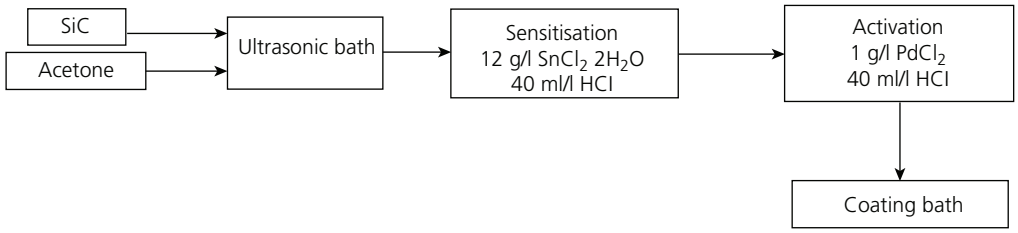


Figure 1. Flow chart of the pretreatment procedure

Ni-P solution	Concentration	Ni-B solution	Concentration
$NiSO_4.6H_2O$	55 g/l	$NiSO_4.6H_2O$	55 g/l
$NiCl_2.6H_2O$	40 g/l	$NiCl_2.6H_2O$	40 g/l
$NaH_2PO_2.H_2O$	20 g/l	$NaBH_4$	3·8 g/l
$Na_3C_6H_5O_7.5H_2O$	120 g/l	$C_2H_8N_2$	60 g/l
NH_3	50 ml/l	NaOH	90 g/l

Table 1. Chemical composition of EN coating

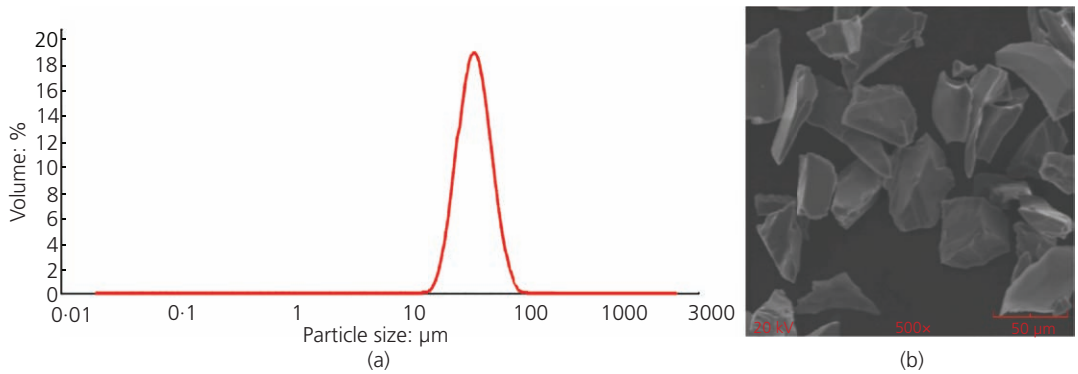


Figure 2. (a) Particle size distribution and (b) SEM morphology of SiC particles

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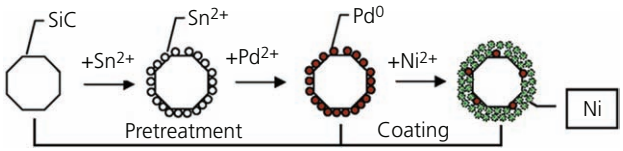


Figure 3. Schematic of pretreatment and coating process

during the coating process, and no stabiliser was used in this study. The composition of solutions used during the electroless Ni-P coating process is listed in Table 1.

Table 1 also lists the chemical composition of electroless Ni-B coating. The solution was maintained at a temperature of 85 ± 2°C with a pH of 12–14. The pH of the plating solution was controlled by adding sodium hydroxide (NaOH). The bath was stirred by a magnetic stirrer during the coating process, and no stabiliser was used, same as with the Ni-P coating.

2.3 Characterisation

The surface morphology of electroless Ni-P- and Ni-B-coated SiC particles were investigated by scanning electron microscopy (SEM) (JEOL JSM-5410), and the composition of the electroless Ni-P-and Ni-B-coated SiC particles was analysed by energy-dispersive spectroscopy (EDS).

3. Results and discussion

3.1 Characterisation of initial SiC powders and coating mechanism

SiC particles with an average particle size of 35 µm and 0·125 m^2/g specific surface area was used in this study. Figures 2(a) and 2(b) show the particle size distribution and morphology of the SiC powders used in this study, respectively. On the basis of the SEM image shown in Figure 2(b), it is possible to indicate that particles have similar morphology, dimension and shape in general.

The nickel coating (Ni-P/B) process on SiC particles can be typically divided into three stages: sensitising of surface, activation and coating. First, Sn^{2+} ions adsorb onto the surface to sensitise the surface of the particle. Afterwards, Pd^{2+} is reduced to Pd^0 according to reaction (1)

$$1.\quad PdCl_2 + SnCl_2 \rightarrow Pd^0 + SnCl_4$$

Thus, particle surfaces gain catalytic activity for the Ni^{2+} to Ni^0 conversion. Figure 3 schematically shows the stages of coating procedure on SiC particles.[23]

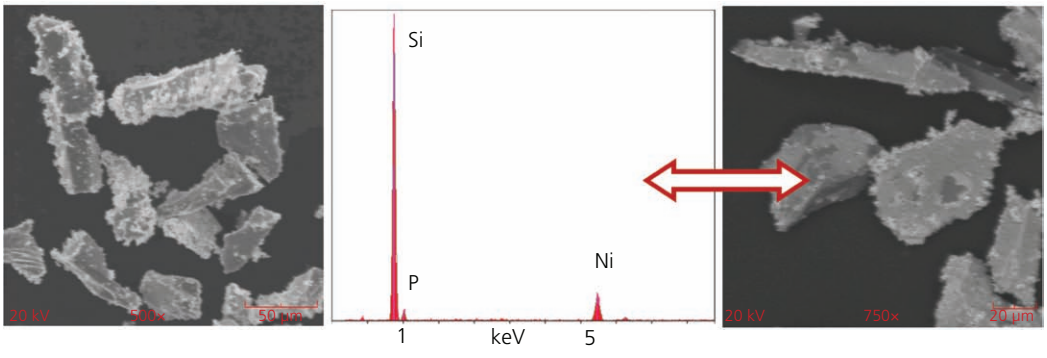
3.2 Ni-P coating

Figures 4(a) and 5(a) show the SEM images of Ni-P-coated SiC powder surfaces that used $NiCl_2.6H_2O$ and $NiSO_4.6H_2O$, respectively, as Ni^{2+} sources. As seen clearly from the figures, the powder surfaces were successfully covered by a continuous Ni-P layer for both Ni^{2+} sources.

High-magnification SEM images in Figures 4(c) and 5(c) showed that electroless coating with the Ni^{2+} source $NiSO_4.6H_2O$ resulted in better surface quality as compared to coating with the Ni^{2+} source $NiCl_2.6H_2O$. Also, EDS analyses of these coatings with different Ni^{2+} sources are shown in Figures 4(b) and 5(b). The EDS analysis indicated that similar nickel and phosphorus peaks were obtained for both coating types. However, the intensity of the nickel and phosphorus peaks obtained by the coating of $NiSO_4.6H_2O$ is higher than the coating of $NiCl_2.6H_2O$.

3.3 Ni-B coating

Figures 6(a) and 7(a) show SEM images of Ni-B-coated SiC powder surfaces that used $NiCl_2.6H_2O$ and $NiSO_4.6H_2O$, respectively, as Ni^{2+} sources. The SiC powders coated with the Ni^{2+} source $NiCl_2.6H_2O$ were more completely covered by the Ni-B coating compared to those coated with the Ni^{2+} source



(a) (b) (c)

Figure 4. (a and c) SEM images of Ni-P-coated SiC powders with the Ni^{2+} source $NiCl_2.6H_2O$. (b) EDS analysis of coated powders shown in (c)

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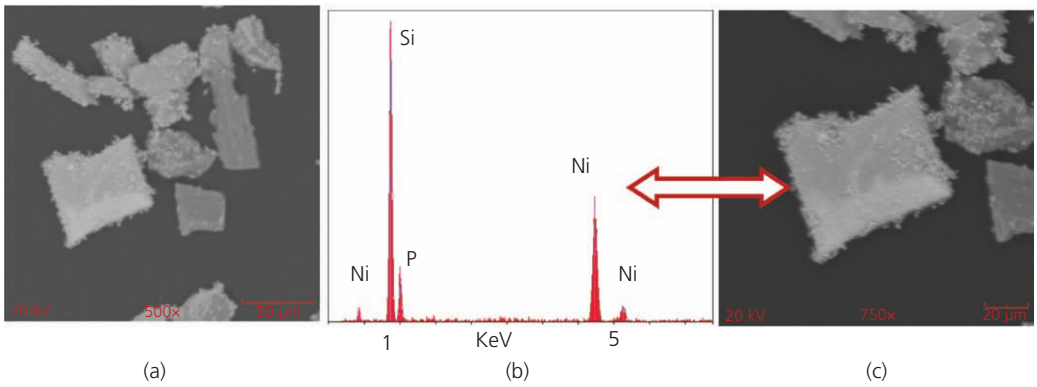


Figure 5. (a and c) SEM images of Ni-P-coated SiC powders with the Ni^{2+} source $NiSO_4.6H_2O$. (b) EDS analysis of coated powders shown in (c)

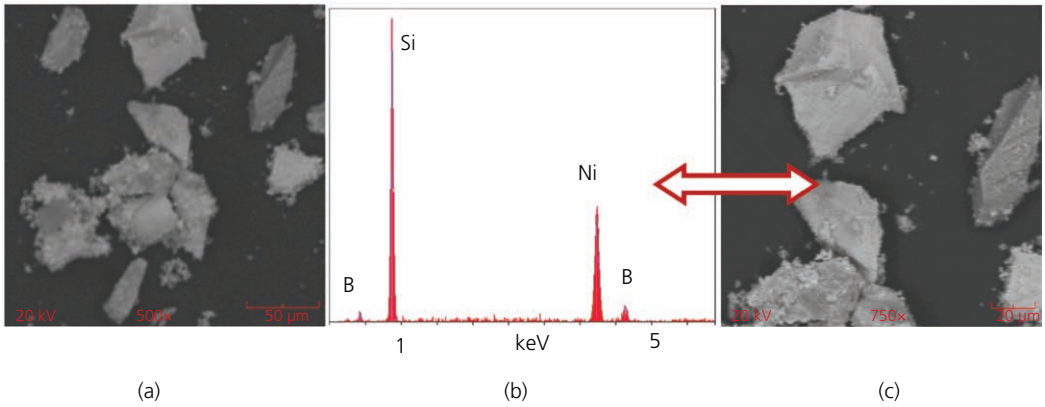


Figure 6. (a and c) SEM images of Ni-B-coated SiC powders with the Ni^{2+} source $NiCl_2.6H_2O$. (b) EDS analysis of coated powders shown in (c)

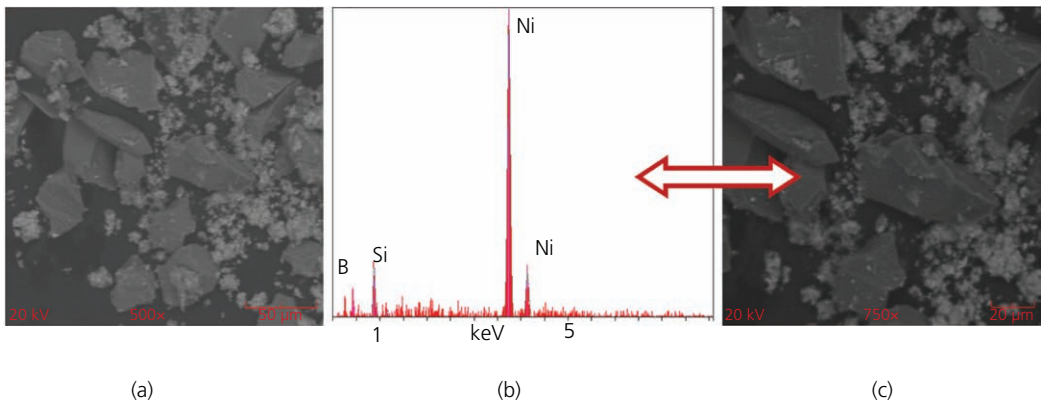


Figure 7. (a and c) SEM images of Ni-B-coated SiC powders with the Ni^{2+} source $NiSO_4.6H_2O$. (b) EDS analysis of coated powders shown in (c)

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$NiSO_4.6H_2O$. In the high-magnification SEM image in Figure 6(c), the coating layer that is obtained with the Ni^{2+} source $NiCl_2.6H_2O$ seems to have better quality and strong bonding in many parts between the coating and the ceramic particles as compared to that shown in Figure 7(c).

However, Figure 7(c) shows that some free Ni particle nucleation occurred on the surface of ceramic powders, and the coating layer on the ceramic surfaces is very thin. The EDS spectra (Figure 6(b) and 6(c)) confirm that the coating layer contains Ni and B, and the coating with Ni^{2+} source $NiCl_2.6H_2O$ has more intensity peaks as compared to the coating with the Ni^{2+} source $NiSO_4.6H_2O$.

4. Conclusion

This study was conducted to evaluate the effects of Ni^{2+} source on the morphology of electroless Ni-P and Ni-B coating of SiC powders. From the experimental results, the following conclusions were obtained

- SiC powders have been electroless coated successfully by Ni-P and Ni-B layer using reducing agents $NaH_2PO_2.H_2O$ and $NaBH_4$, respectively, in the presence of two different Ni^{2+} sources, namely $NiSO_4.6H_2O$, $NiCl_2.6H_2O$.
- It was shown that a better uniformity and bonding were obtained for Ni-P coatings with the Ni^{2+} source $NiSO_4.6H_2O$ as compared to $NiCl_2.6H_2O$.
- For Ni-B coatings, the Ni^{2+} source $NiCl_2.6H_2O$ provided better quality and continuous coating layer on SiC surfaces.
- The EDS results confirmed that the chemical analysis of electroless deposition layers on SiC powders consist of Ni-P and Ni-B depending on the used reducing agents.
- SiC particles coated with Ni-P and Ni-B layers can be evaluated as a useful reinforcement for possible MMC production.

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