

# Preparation of nickel-coated powders as precursors to reinforce MMCs

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The preparation of nickel-coated ceramic particles as precursors for MMC fabrication was studied.  $\text{Al}_2\text{O}_3$  and SiC powders of three different particle sizes were successfully coated with Ni using an electroless metal plating technique. Uniform and continuous nickel films were deposited on both, alumina and silicon carbide powders, with a final composition ranging from 1.6 to 1.9 wt% phosphorus, 18–21 wt% of metallic nickel and the balance is ceramic. XRD showed that the Ni-P deposit was predominantly amorphous. However, after heat treatment, the metallic deposits crystallize into Ni and  $\text{Ni}_3\text{P}$  phases, as confirmed by DSC analyses. Preliminary results showed that the use of Ni-coated powders enhances the wettability between the matrix and ceramic phase when processing particulate MMCs by infiltration techniques. The coating promoted easy metal flow through the preform, compared to the non-infiltration behavior of the uncoated counterpart samples.

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## 1. Introduction

The combinations of properties of SiC/Al and  $\text{Al}_2\text{O}_3/\text{Al}$  composites make them attractive structural materials. However, their preparation still suffers from several difficulties. One problem is the high reactivity of aluminum with silicon carbide to form aluminum carbide that results in reinforcement degradation and reduction in strength of the composite. Another difficulty is the low wettability between ceramics and liquid metals. In order to reduce the SiC/Al interaction and promote wetting between  $\text{Al}_2\text{O}_3$  reinforcements and molten aluminum during processing, the ceramic surface can be modified by deposition of metal coatings using different techniques [1, 2].

A variety of processing schemes for producing MMCs relies on infiltrating liquid metals or alloys into porous ceramic bodies. Since spontaneous infiltration is governed by the wettability of the ceramic by the metal, it is recognized that infiltration can be promoted by improving the wetting between both phases by modifying the particulate-reinforcement surface using a metal coating [3, 4]. Generally speaking, a moderate chemical interaction improves wetting, assists liquid-phase fabrication of the composite and enhances the strength of the interface. A potential metal for such coatings is nickel [5–8].

Autocatalytic metal plating represents an easy and effective method for plating of parts since a variety of metals can be used and a thick coating can be formed [9]. Moreover, the coating can be plated onto either nonconductive or conductive surfaces that do not share electrical continuity [10–13]. Electroless nickel is an engineering coating normally used because of its excel-

lent corrosion and wear resistance. However, in recent years nickel films plated on reinforcements have been used to improve the adhesion and wettability during composite fabrication [5–8]. Electroless nickel coatings are produced by controlled chemical reduction of nickel ions onto the catalytic surface. The deposit itself is catalytic to reduction, and the reaction continues as long as the surface remains in contact with the electroless nickel solution. The process yields a uniform coating over all surfaces, regardless of size and shape.

In spite of the importance of wettability in the manufacturing of composites, relatively few studies have been conducted to enhance the infiltration rate by metal coating of reinforcements. In the present study, as a first stage in the fabrication of metal matrix composites, the work was aimed at establishing the best processing route to achieve efficient metal-deposition on ceramic powders. The quantity of deposited material, and the uniformity and nature of the coating through deposition of Ni on  $\text{Al}_2\text{O}_3$  and SiC particles were determined. The wetting behavior between Ni-coated substrates and liquid aluminum, as well as the application of the composite powders obtained as precursors for reinforcing MMCs by infiltration techniques will be presented in a future paper.

## 2. Experimental

### 2.1. Materials

The materials employed were pure SiC (97% min., Crystolon, *Norton Silicon Carbide*) and high purity  $\text{Al}_2\text{O}_3$  (99.55%, 38 Alundum, *Norton Materials*) powders. Autocatalytic nickel plating was performed on

TABLE I Basic properties of SiC and Al<sub>2</sub>O<sub>3</sub> particles

	Norton SiC			Norton Al <sub>2</sub> O <sub>3</sub>		
	180	240	400	180	240	400
Grit Size	180	240	400	180	240	400
True Density g cm <sup>-3</sup>	3.2	3.2	3.2	3.95	3.95	3.95
Particle Size <i>D</i> <sub>50</sub> (μm)	78	49	18	74	46	17
Surface Area* m <sup>2</sup> g <sup>-1</sup>	0.090	0.118	0.315	0.091	0.133	0.322

(\*) BET single point method.

three different particle size powders namely 180, 240 and 400 grit. The characteristics of the ceramics used are listed in Table I.

## 2.2. Coating procedure

In the present study, usually 100 g of powder were processed for cleaning and activation using the following procedure:

1. Particle surface soak-cleaned by immersing in acetone with ultrasonics.
2. Cleaning and microscopic roughening in HNO<sub>3</sub>.
3. Sensitization in a solution containing stannous chloride (SnCl<sub>2</sub>) and HCl.
4. Activation using a palladium chloride (PdCl<sub>2</sub>) solution.

Thorough rinsing was required between the different treatment stages to prevent contamination of the solutions. Furthermore, the powders were occasionally stirred gently and maintained in an ultrasonic bath to enhance the chemical process.

The electroless nickel deposition bath was developed and refined using formulations given in the literature [5, 10, 12–15]. The bath composition is given in Table II. The proportion of elemental powders that added to the plating bath was 15 g per liter, and with continuous stirring, all of the particles were exposed to the electroless nickel solution. The bath was operated under acid conditions and high temperature; the powders were plated at 85 °C and 90 °C and the pH adjusted to 5.0, 5.5 and 6.0 using NaOH. The plating time ranged from 10 to 40 minutes.

The morphology of the coating was examined using scanning electron microscopy. Energy dispersive X-ray spectroscopy (EDS) was helpful in identifying the metal-coating layers and its components. A pre-defined amount of the composite powder was immersed in a known volume of high-purity HNO<sub>3</sub> until complete dissolution of the metal film. The solution was precision diluted to suitable concentration for inductively coupled plasma-atomic emission spectroscopy (ICP-

TABLE II Composition of the electroless nickel bath

Nickel chloride, hexahydrate	NiCl <sub>2</sub> ·6H <sub>2</sub> O	30 g L <sup>-1</sup>
Sodium succinate, hexahydrate	Na <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>4</sub> ·6H <sub>2</sub> O	10 g L <sup>-1</sup>
Glycin	H <sub>2</sub> NCH <sub>2</sub> COOH	10 g L <sup>-1</sup>
Sodium hypophosphite, monohydrate	NaH <sub>2</sub> PO <sub>2</sub> ·H <sub>2</sub> O	20 g L <sup>-1</sup>
Lead nitrate	Pb(NO <sub>3</sub> ) <sub>2</sub>	2 mg L <sup>-1</sup>

AES). From these studies, the composition and weight of the deposits were calculated. Phase analysis of the coating was studied using X-ray diffractometry. DSC thermograms were obtained for the as-plated alumina and silicon carbide powders using a 10 K min<sup>-1</sup> scan rate in order to determine phase transformation of the Ni-P deposits.

## 3. Results and discussion

Characterization of the Ni-coated particles is necessary to determine the amount, chemical nature, morphology, uniformity and distribution of the metal coating on the powders. SEM examination of the starting powders revealed that SiC particles have a granular form for the three different sizes used, while alumina samples exhibited predominantly angular shapes with sharp edges.

The particle size (*D*<sub>50</sub>) quoted by the manufacturer (Table I) shows that silicon carbide particles are slightly larger than the alumina, in spite of the fact that the powders are labeled with the same grit sizes. From cumulative particle size distribution determination, a narrower size distribution was detected for silicon carbide, while alumina powders showed a relatively wider particle size distribution. Hence, a slightly higher surface area was confirmed for alumina samples using BET analysis, mainly because of the presence of small powder aggregates surrounding the large particles (Table I).

### 3.1. Nickel plating on SiC and Al<sub>2</sub>O<sub>3</sub> powders

The performance of the autocatalytic nickel coating depends largely on the surface finish of the substrate to be plated. The chemistry of the electroless nickel bath requires closer control than that of most other types of plating baths. To avoid contaminating the bath and to ensure adequate coating adhesion and initiate deposition, every particle was cleaned, microetched, and surface catalyzed prior to plating. The Pd-activation procedure assured elimination of the passive condition of the surfaces, making them suitable for electroless plating due to the presence of chemically deposited Pd nuclei that initiate nickel deposition. The activation process was characterized by a change in color from the light red of PdCl<sub>2</sub> activating solution, to a dark brown solution after powder immersion.

Autocatalytic nickel deposition was performed using sodium hypophosphite as the reducing agent (Table II), giving electroless nickel deposits along with a simultaneous deposition of phosphorus from the electroless bath. Therefore, the electroless nickel deposit was a Ni-P alloy, as confirmed by EDS examination. A maximum deposition rate on ceramic powders occurred at near to pH 5.5, irrespective of plating temperature, and the metal content of the electroless nickel deposits was slightly higher at 90° than at 85 °C. Such powders are inherently heterogeneous, in that each particle consists of a core of ceramic material and a metallic coating.

Contrary to expectations, plating time did not show an increase in the nickel deposition rate (Fig. 1). This is attributed to the fact that the electroless bath has become exhausted due to the limited amount of the Ni-plating solution compared with the large surface to be

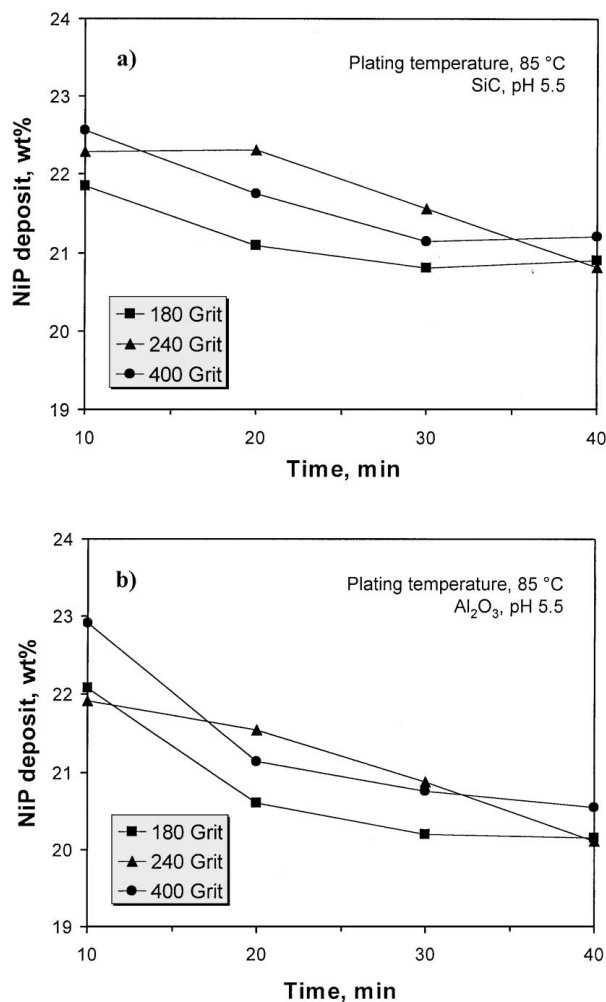


Figure 1 Effect of plating time on the nickel deposition on silicon carbide particles.

plated. Additionally, the pH of the acidic solution was altered with the progress of the plating process: during deposition, byproducts of the reaction, orthophosphite ( $\text{HPO}_3^{2-}$ ) and hydrogen ions accumulate in the solution, affecting the chemistry of the plating bath. Such events were characterized by a reduced gas evolution from the bath and an excessive decoloration of the electroless solution. Furthermore, the prolonged stirring could induce a debonding of fine Ni-particulates adhered to the outer surface of the deposit, thus leading to a slight decrease of the amount of deposit. The deposition behavior was similar for both silicon carbide and alumina powders, in that the Ni-P deposits ranged from 20 to 23 wt% of the bulk Ni-coated powders, irrespective of the particle size.

Table III resumes the change of phosphorus content in the metallic coating as a function of time. The phos-

TABLE III Phosphorous content in the metallic film for coarse Al<sub>2</sub>O<sub>3</sub> and SiC powders as a function of time

Plating Time (min)	Phosphorous content (wt%)	
	Ni-Al <sub>2</sub> O <sub>3</sub>	Ni-SiC
10	8.35	8.36
20	8.73	8.63
30	8.62	8.81
40	9.23	8.91

phorus content on the deposits increased slightly with plating time because of the tendency of the bath components to decompose as plating time elapses. Therefore, the formation of orthophosphite ion ( $\text{HPO}_3^{2-}$ ) leads to higher phosphorus content on the outer rather than the inner layers of the deposit. However, it was maintained between 7 and 9 wt% of the total electroless nickel deposit, depending on the plating conditions. Furthermore, a higher co-deposition of phosphorus was observed on the fine rather than on the coarse particles. This is because the large surface of the fine powder leads to a self-accelerating chain reaction and decomposition, which was manifested by an extensive bubbling due to increased hydrogen gas evolution.

The composition of the bulk Ni-coated powder deposits determined by ICP-AES analysis ranged from 1.6 to 1.9 wt% for the phosphorus content, 17–21 wt% of metallic nickel, and the balance is ceramic. The theoretical density of the coating and thus, the density of the bulk Ni-coated composite powders were evaluated through the rule of mixtures. From the chemical composition, the calculated density for the Ni-film ranged from 7.8 to 8.0 g cm<sup>-3</sup>, while the bulk density of the Ni-coated Al<sub>2</sub>O<sub>3</sub> powders was near to 4.3 g cm<sup>-3</sup>, compared with 3.6 g cm<sup>-3</sup> for Ni-coated SiC. The difference in density for the coated-powders is essentially due to the difference in density of the ceramic cores, as the slight variation in composition of the deposits did not alter significantly the computed density. The coating thickness for both ceramics varied from 0.5 μm for the fine to 1.5 μm for the coarse powders (Fig. 2).

Typical surface morphologies of uncoated and Ni-coated SiC powders are shown in Fig. 3. While the as-received powders show a clean, deposit-free surface (Fig. 3a), the plated powders show a uniformly distributed nickel coating (Fig. 3b). At high magnification, a continuous nickel film is observed over the whole surface; the coating is present on all regions of the particles regardless of size and shape (Fig. 3c, d). Plating led to an increase in the surface area of the starting particles, so that for example, the specific surface area of the original fine SiC powder went from 0.315 m<sup>2</sup> g<sup>-1</sup> to 0.978 m<sup>2</sup> g<sup>-1</sup> after Ni-plating. These

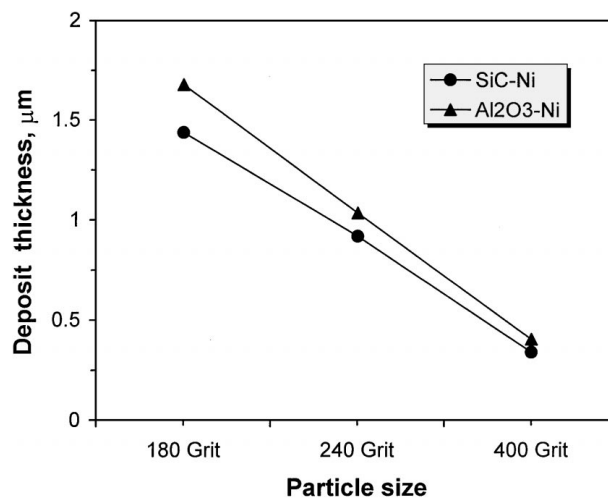


Figure 2 Electroless nickel deposit thickness as a function of particle size for alumina and silicon carbide powders.

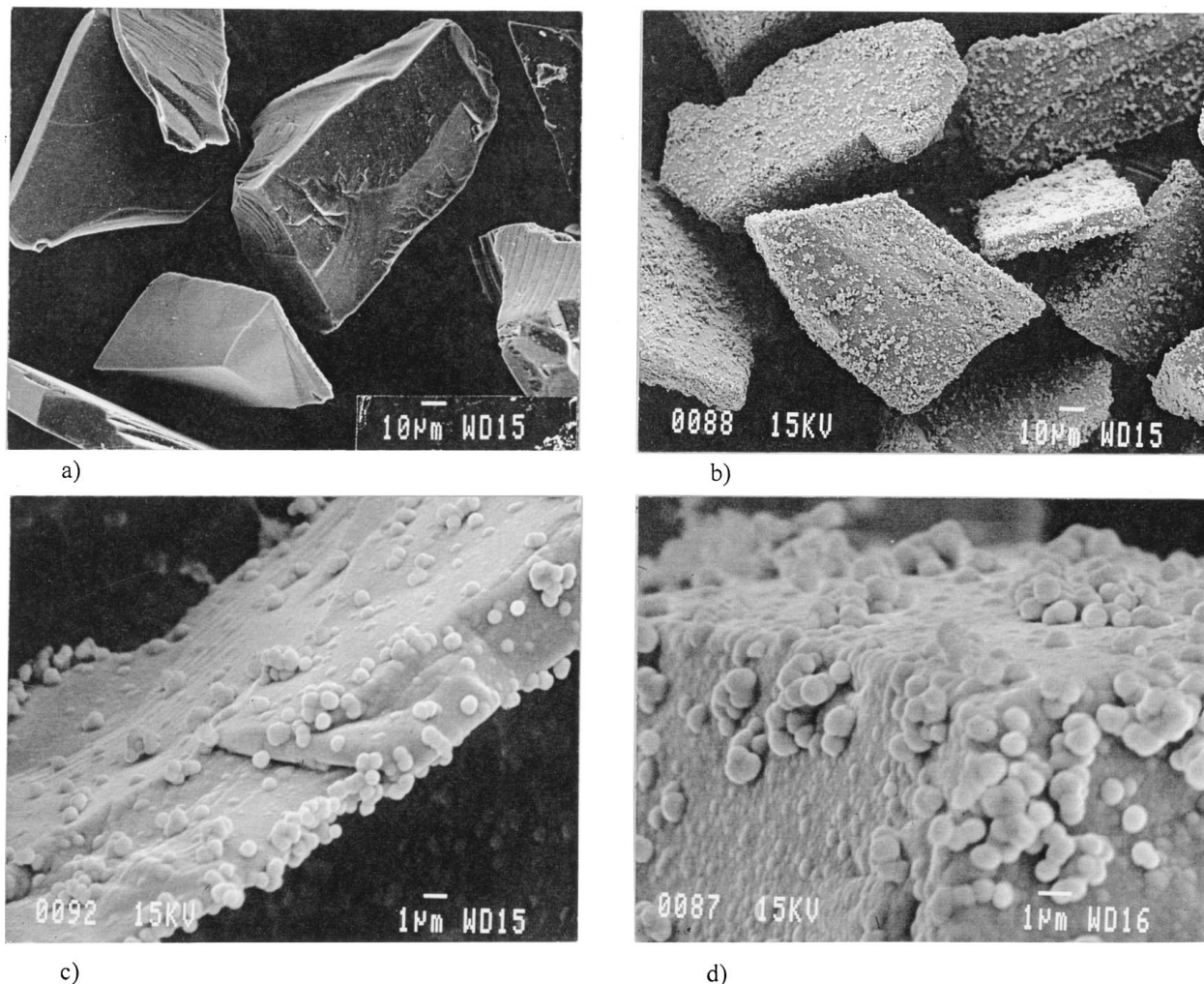


Figure 3 Surface morphology of (a) uncoated and (b) Ni-coated silicon carbide powders. High magnification micrographs of (c) Ni-coated alumina and (d) Ni-coated silicon carbide.

results are attributed to the fine nickel particles  $\sim 1 \mu\text{m}$  found on the outer layer of the deposit and the presence of microvoids between the fine-trapped particles.

The literature suggests that electroless nickel deposits, which have not been heat-treated, can have structures ranging from extremely small crystallites to those that are fully amorphous. In this study, the coated powders were essentially amorphous in the as-plated condition, which is consistent with previous studies in which alloys containing more than 8 wt% phosphorus were found predominantly amorphous [12, 14].

Fig. 4 shows three X-ray traces related to the as-received, as-plated, and heat-treated nickel coated SiC powders. X-ray diffraction patterns of the as-plated powders (Fig. 4b) showed a pronounced broad band in the region corresponding to the Ni (111) and (200) reflections, signifying that this particular deposits contains the metal in an amorphous state. The figure also shows sharp peaks corresponding to silicon carbide, as well as a noisy background, characteristic of an amorphous structure. All the deposits, upon heat treatment at  $400^\circ\text{C}$ , transformed into a mixture of crystalline Ni and  $\text{Ni}_3\text{P}$ . Examination of the coating structure of the heat-treated powders revealed a metal film showing an excellent degree of conformity to the ceramic surface. X-ray diffraction traces obtained from these samples showed sharp, well-defined peaks

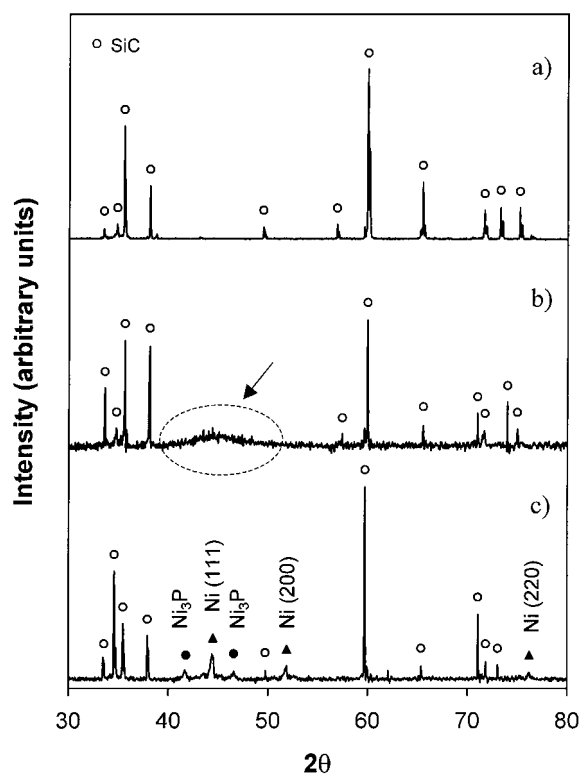


Figure 4 XRD patterns of (a) as-received, (b) as-coated, and (c) heat-treated silicon carbide.

corresponding to a fully crystallized structure (Fig. 4c). The peaks can be assigned to either face-centered cubic nickel or the tetragonal Ni<sub>3</sub>P phase, the most-prevalent nickel phosphide in the deposits. Structural characteristics of the as-plated and heat-treated deposits on alumina powders were found similar to those observed in the silicon carbide samples. Therefore, it is clear that the amorphous character shown in the as-plated powders becomes crystalline after heat treatment, revealing deposits containing the stable Ni and Ni<sub>3</sub>P phases.

Differential scanning calorimetry was performed on both the nickel coated SiC and Al<sub>2</sub>O<sub>3</sub> powders at a scan rate of 10 K min<sup>-1</sup>. Table IV presents the values of the peak temperature and heat evolved ( $\Delta H$ ) derived from the DSC study. The thermograms revealed that the amorphous Ni-P structure exhibited a crystallization temperature around 345 °C. As can be seen from Fig. 5, the curves exhibit only a single irreversible solid-state exothermic transformation peak; both of the samples presented a similar exotherm in the temperature range of 325–375 °C. Considering the XRD results after heat-treatment, and in agreement with the results published by other authors [15], the maximum energy of the exothermic reaction peak at 345 °C may, therefore, be ascribed to the crystallization of the amorphous deposits into Ni and Ni<sub>3</sub>P. An additional high-temperature peak at about 405 °C that is attributed to the growth

TABLE IV Calorimetric data and peak temperature for Ni-coated Al<sub>2</sub>O<sub>3</sub> and SiC powders

Deposit	<i>T</i> (°C)	$\Delta H$ (J kg <sup>-1</sup> )
Ni-SiC	345.3	6730
Ni-Al <sub>2</sub> O <sub>3</sub>	343.9	5170

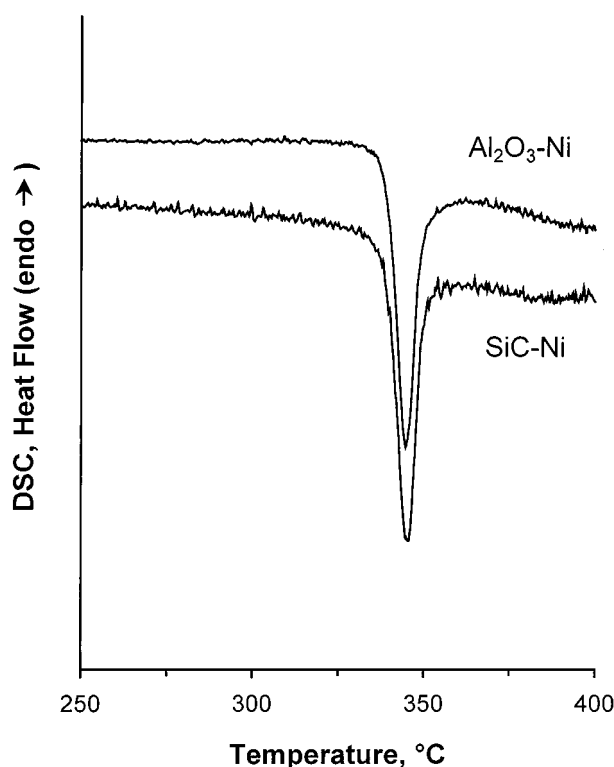
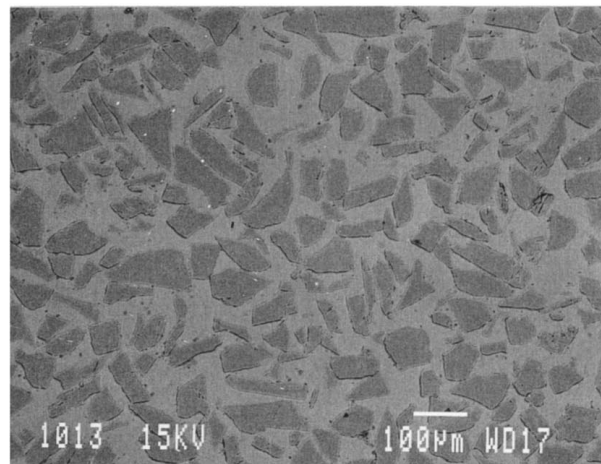


Figure 5 DSC scans of as-deposited (a) SiC, and (b) Al<sub>2</sub>O<sub>3</sub>, scan rate 10 K min<sup>-1</sup>.

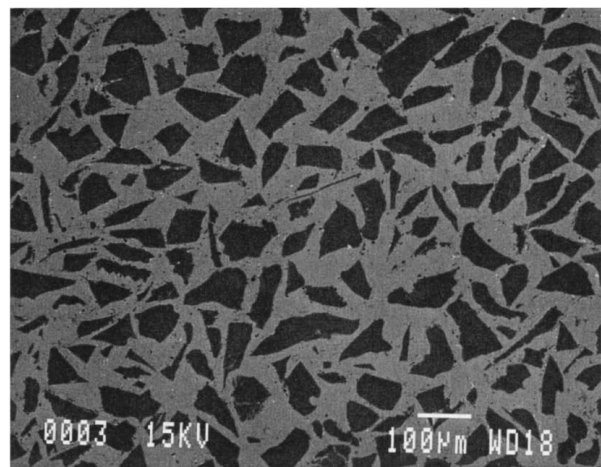
of Ni<sub>3</sub>P has been also reported [15]. However, in the present study this peak was not observed. The crystallization and growth peaks probably coincided.

Using a vacuum infiltration technique, the effect of nickel deposition on the infiltration behavior of particulate preforms with liquid aluminum was investigated. As-plated and deposit-free powders were infiltrated with commercially pure aluminum at 800–900 °C. Preliminary results confirmed the favorable effect of surface modification during composite processing. It was concluded that the metallic coating improved the wettability of ceramics, promoting easy metal flow through the preform in comparison to the non-infiltration behavior of the uncoated counterpart samples. At the same time, it changed the matrix composition by alloying with the matrix.

Particulate composites reinforced with nickel-coated SiC or Al<sub>2</sub>O<sub>3</sub> were fabricated at 900 °C in less than two minutes, while in the case of the as-received powders, no infiltration was observed after 20 minutes under similar experimental conditions. Fig. 6 shows characteristic microstructures of these composites; the nickel coated samples provided wetting conditions, giving porosity-free components with a homogeneously distributed reinforcing phase in the metallic matrix, consisting of aluminum and aluminum-nickel compounds. No apparent



a)



b)

Figure 6 SEM micrographs of infiltrated samples from nickel-coated powders. (a) SiC/Al composite, and (b) Al<sub>2</sub>O<sub>3</sub>/Al composite.

interfacial reaction between the matrix and the ceramics was detected. Thus, the formation of the detrimental  $Al_4C_3$  was avoided in these composites reinforced with silicon carbide particles.

A complete study on the wetting behavior between Ni-coated ceramics and liquid aluminum, as well as the application of the composite powders as precursors for reinforcing MMCs will be presented in a future paper. The infiltration kinetics of the components as a function of the processing parameters and the properties of such composites will be also included.

#### 4. Conclusions

To enhance the wettability of the ceramic phase for composite fabrication,  $Al_2O_3$  and SiC powders of three different particle sizes were successfully coated with Ni in order to prepare preforms for infiltration with molten aluminum. Uniform and continuous nickel films were deposited on both, alumina and silicon carbide powders, with a final composition ranging from 1.6 to 1.9 wt% phosphorus, 17–21 wt% of metallic nickel and the balance is ceramic. XRD showed that the structure of Ni-P coating was predominantly amorphous. The deposits, upon heat treatment at 400 °C, transformed into a mixture of mainly crystalline Ni and  $Ni_3P$ , as confirmed by XRD. All the deposits gave a single exothermic peak in the DSC study due to the crystallization of the amorphous coating, with a crystallization temperature around 345 °C. Preliminary results on the infiltration of Ni-coated powders with molten aluminum shows that the powders are suitable as reinforcing materials for fabricating particulate aluminum matrix MMC.

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