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Metal-coated colloidal particles

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Procedures are described for coating of submicrometre ceramic powders with copper and nickel. The process required precoating of the core particles with a palladium catalyst. A precoating procedure was developed in which palladium chloride is reduced by sodium hypophosphite or stannous chloride on the powder surface in aqueous suspensions. Commercial electroless solutions were used to deposit copper and nickel on the catalysed powders. The effect of various experimental parameters on the effectiveness of the surface conditioning of the particles was also investigated.

1. Introduction

The need for metal-coated fine powders has recently been recognized in the areas of composite materials. In the processing of metal-matrix composites, poor wetting of the ceramic particles with the molten metal often results as a consequence of the incompatibility between the covalent or ionic nature of the ceramic surface and the metallic nature of the matrix. Improved wetting characteristics were obtained when the dispersoids were initially coated with metals [1–8]. When ceramic powders are incorporated in metal matrices by powder metallurgy, melt infiltration, or mixing with molten/semi-molten metal, an inhomogeneous distribution of the ceramic component often results. Uniform distribution becomes increasingly difficult with higher volume fraction of the ceramic particulates. For the fabrication of metal-matrix composites with high ceramic-particle content, the dispersed phase can be coated with appropriate amounts of the desired matrix metal, and compacted to produce a dense body with a relatively homogeneous distribution of the ceramic component.

The electroless deposition of copper or nickel on non-metallic objects usually requires catalysis of the surfaces to be coated. The activation of macroscopic surfaces is often achieved using palladium or Pd–Sn catalysts available as a suspension of colloidal particles in the submicrometre–micrometre size range [9].

The encapsulation of fine, non-metallic powders with copper or nickel also requires heterogeneous catalysis. Unfortunately, the commercial palladium or Pd–Sn catalysts, owing to their particulate nature, are unsuitable to treat submicrometre core particles: the two kinds of particle can at best heterocoagulate and the effectiveness of the catalyst layer deposited would be greatly influenced by the relative sizes of the core and the catalyst particles.

Current techniques for electroless metal deposition on non-metallic powders usually involve relatively coarse core particles [2–5]. Moreover, the catalysis treatment is multi-step, requiring transfer of the particles between several baths. In addition, little attention has been paid to enhance the stability of the suspension during micro-encapsulation. Maintaining dispersion stability becomes particularly difficult with extremely fine particles, especially when even a small weight fraction of the solids, corresponding to a very large particle number concentration, renders the average interparticle distance extremely small.

The typical process for palladium treatment of particles is carried out in two steps [10]. First, the core particles are sensitized by immersion in an aqueous solution of stannous chloride containing hydrochloric acid. The particles are then isolated and activated by dispersing in an aqueous solution of palladium chloride and hydrochloric acid. The solids are again recovered from the activation bath, and contacted with electroless coating solutions of copper or nickel. The complexities of particle recovery from the various baths between steps dramatically increase with decreasing particle size. Thus, for the catalysis of submicrometre particles, reduction in the number of steps can mean a saving in the corresponding equipment and operating costs.

In this work, a one-step process for the precoating of the core particles with palladium catalyst has been developed in which powdered silicon nitride and silicon carbide of various morphologies, alumina, titania, and a vinylidene copolymer, were catalysed successfully. A process for catalyst pre-coating using stannous chloride as a reducing agent was also developed. Commercial electroless solutions were used to deposit copper on the catalysed powders. Copper-coated silicon carbide powders were consolidated to fabricate a composite material.

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2. Experimental procedure

2.1. Materials

Aqueous solutions of palladium chloride (Aldrich, USA), stannous chloride (Aldrich, USA) and sodium hypophosphite (Mallinckrodt Chemical Company, USA) were used for catalysis of colloidal silicon nitride powder (Superior Graphite, USA, Toshiba Ceramics, Japan) and whisker (UBE Industries (America), Inc.); silicon carbide powder (Superior Graphite, USA), platelets (American Matrix, Inc., USA; Darvan 820, W. R. Grace & Co., USA) and whisker (American Matrix, Inc., USA); titania (MCB Reagents, USA), alumina (Alcoa, USA), and a vinylidene copolymer (Darvan 820, W. R. Grace & Co, USA). Commercial electroless solutions were used to deposit copper (LC-A and LC-B Solutions, M & T Chemicals, Inc., USA) and nickel (Niklad 795, Witco, Allied-Kellite Division, USA) on the catalysed core particles. The suspensions were stabilized during microencapsulation by the addition of polymethacrylates or polymethacrylic acid. (Daxad Dispersants, W. R. Grace & Co., USA).

2.2. Catalysis of the non-metallic core powders

2.2.1. Treatment with palladium catalyst by hypophosphite reduction

In this method the silicon nitride particles (Toshiba ceramics, Japan) are catalysed with palladium by the reduction of palladium chloride by sodium hypophosphite. The untreated solids were suspended in an aqueous solution of palladium chloride and ammonium hydroxide at a pH of 2.5–3. A solution of sodium hypophosphite was then added, and ageing was carried out with mild stirring for 1–15 min at 25–60 °C. The effect of experimental parameters such as pH, concentration of palladium chloride, and concentration of the core particles on the catalytic activity of the treated powders was investigated. The ranges of these parameters were pH 2.5–10, palladium chloride 40–400 $\mathrm{mg\,l^{-1}}$ and core particles 20–140 $\mathrm{g\,l^{-1}}$. The concentration of sodium hypophosphite was typically 0.1–0.4 $\mathrm{g\,l^{-1}}$. The resulting suspension was concentrated by sedimentation of the solids and decanting of the supernatant. This concentrated suspension can be used directly in the subsequent encapsulation step.

The pH of the palladium pre-coating bath appeared to be a critical factor influencing the success of the catalysis process. To determine the effect of this parameter, a two-part investigation was carried out. In the first part, "blank" solutions, free of core particles, were studied. In the second, the core particles were incorporated into the systems.

The blank systems were prepared at room temperature with 50 $\mathrm{cm^3}$ solutions of $\approx 0.1\ \mathrm{g\,l^{-1}}$ palladium chloride, to which 0.1 $\mathrm{cm^3}$ 30% hydroxide was added. The pH was adjusted to 2.5–3 by the addition of ammonium hydroxide or hydrochloric acid. To the resulting solution, $5 \times 10^{-2}\ \mathrm{cm^3}$ 500 $\mathrm{g\,l^{-1}}$ $NaH_2PO_4 \cdot 2H_2O$ solution was added during rapid magnetic stirring.

The colloidal Pd–Sn catalyst preparation procedure described by Shipley [11] was extended to the treatment of submicrometre silicon carbide powders. The original formulation consisted of 1 g palladium chloride ($PdCl_2$), 60 $\mathrm{cm^3}$ hydrochloric acid (HCl, 37%), 22 g stannous chloride, ($SnCl_2 \cdot 2H_2O$), and water to make ≈ 1 litre.

In one litre of water containing the hydrochloric acid, the palladium chloride and the stannous chloride were dissolved in order. This solution, when aged at room temperature for about 1 week, yielded a Pd–Sn catalyst hydrosol.

For the surface treatment of the silicon carbide powders, an aqueous suspension containing 100 $\mathrm{g\,l^{-1}}$ solids was prepared. The pH was adjusted to a value corresponding to the dilute acid prepared by adding 60 $\mathrm{cm^3}$ 37% HCl to 1 litre deionized water. The palladium chloride and stannous chloride, in order, were then dissolved in the suspension. Finally, the dispersion was aged with mild stirring at 50–60 °C overnight. In the next step, the catalysed particles, recovered from the resulting suspension by sedimentation, were washed with 10^{-2} M HCl. In some cases, the solids were also washed with deionized water. Finally, the surface-treated powders were dried at 60 °C overnight.

Because this is a two-step process, in contrast to the two-step hypophosphite reduction process, only limited experiments were conducted to investigate the activation of ceramic particles with Pd–Sn catalysts.

2.3. Microencapsulation with copper

To a concentrated suspension containing $\approx 200\ \mathrm{g\,l^{-1}}$ catalysed powders, ammonium polymethacrylate (Daxad-32), and aliquots of deionized water and electroless copper solutions LC-B and LC-A were added in order. The final suspensions contained $\approx 5\ \mathrm{g\,l^{-1}}$ Daxad dispersant. The dispersions were stirred magnetically, and the "extinction time", defined as the time taken for the disappearance of the blue colour from the suspension medium, was measured. This semi-quantitative extinction time was taken as an indicator of the rate of copper coating – the shorter the duration, the faster was the deposition of copper.

2.4. Microencapsulation with nickel

The silicon nitride powders, catalysed as described later in Fig. 2, were tested for coating with nickel. To 50 $\mathrm{cm^3}$ electroless nickel-coating solution, prepared by dilution as recommended by the supplier and preheated to 75 °C, 0.8 g activated core particles were added during magnetic stirring. The ageing was carried out until the suspension turned from grey to black in colour.

2.5. Consolidation of the powders

The coated silicon carbide particles containing 72 wt% copper, after drying, appeared black due to oxidation of the metal layers. The solids, reduced in Ar–5%H_2 at 250 °C for 1 h, had the characteristic colour of copper. The powders were uniaxially pressed into 9.53 mm ($\frac{3}{8}$ in) diameter cylindrical pellets at

51 MPa (7500 p.s.i.), and cold isostatically pressed at 680 MPa (100 000 p.s.i.) for 3 min. The final pellets, annealed in argon at 500 °C, were characterized for density, hardness and microstructure.

3. Results

3.1. Catalysis of the core powders

3.1.1. Treatment with palladium catalyst by hypophosphite reduction

The blanks with pH ≥ 4 abruptly became dark within 45 s of the hypophosphite addition. In about 90 s, the system flocculated to yield black particles that settled rapidly. The observed instability of the baths indicated that pH ≥ 4 may not be suitable for the catalysis of ultrafine ceramic particles. At pH 3, the appearance of a dark colour was less sudden than at pH 4, and the palladium hydrosol produced was stable towards agglomeration for a few hours. When the initial pH was reduced to 2.5, the colour transition was very gradual. The dark colour appeared in 2–4 min, and a relatively stable dispersion of palladium was produced. The observations indicated the choice of pH 2.5–3 for the palladium treatment of submicrometre powders using hypophosphite reduction. At pH 2.5, the reduction process was accelerated by heating the blanks to 45 °C without adversely affecting the stability of the resulting hydrosol.

The procedure for the catalysis of silicon nitride core particles at pH ≥ 4 was not effective (dispersion of the treated particles in electroless copper solution was chemically stable for 12 h). When the catalyst precoating was carried out at pH 2.5–3, the core particles could be successfully coated with copper. For a given set of experimental conditions, the extinction time was found to be relatively constant when the particles were catalysed at pH 2.5–3.

The ammonium hydroxide in the dispersant Daxad 32 neutralized the acid in the low pH core particle catalysis suspensions. No washing of the catalysed powders was required prior to microencapsulation with copper. Although the dispersant did not significantly affect the stability of the suspensions containing water and electroless solution LC-B, the Daxad-containing dispersions deflocculated when electroless solution LC-A was added. Substantial agglomeration was observed in systems where the copper deposition was carried out in the absence of Daxad.

Fig. 1 is a plot of extinction time as a function of palladium chloride concentration, other experimental parameters being the same. It was observed that the palladium chloride concentration has a marked influence on the success of the catalysis process. The extinction time decreased rapidly, and then became relatively constant as the palladium chloride concentration was gradually increased.

A strong dependence of extinction time on the concentration of core particles in the catalysing suspension was also observed, as is presented in Fig. 2. The extinction time, relatively constant at low particle concentrations, increased sharply and then became relatively constant as the core particle concentration was systematically increased while keeping other factors the same. The extinction time was found to decrease with increasing core particle concentration in the copper coating solutions, as is shown in Fig. 3.

Table I includes the data on the extinction times for various combinations of silicon nitride and palladium chloride concentrations, for a fixed $PdCl_2/Si_3N_4$ ratio. It is observed that the extinction is significantly influenced by the actual concentrations of the core particles and palladium chloride, although the relative amounts of the two substances may be the same.

The effectiveness of the catalysis procedure was tested for several types of core particle. The powder treatment was carried out by suspending 2 g particles in 50 cm^3 suspensions under the conditions described in Fig. 2. The length of the extinction time for the various types of systems, reported in Table II, varies significantly with the nature and geometry of the core particles.

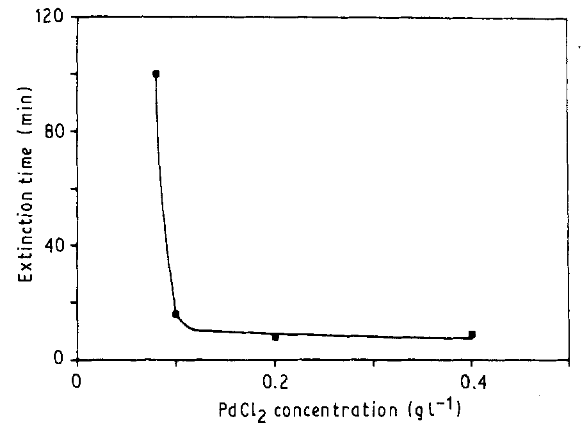

Figure 1 Plot of extinction time for silicon nitride particles catalysed in 50 cm^3 aqueous suspensions of (initial) pH 3, containing various amounts of palladium chloride, 0.1 cm^3 30% ammonium hydroxide, 40 g l^{-1} core particles and 0.2–0.4 g l^{-1} sodium hypophosphite, stirred at 45–50 °C for 15 min. The copper coating bath contained 27 g l^{-1} core particles.

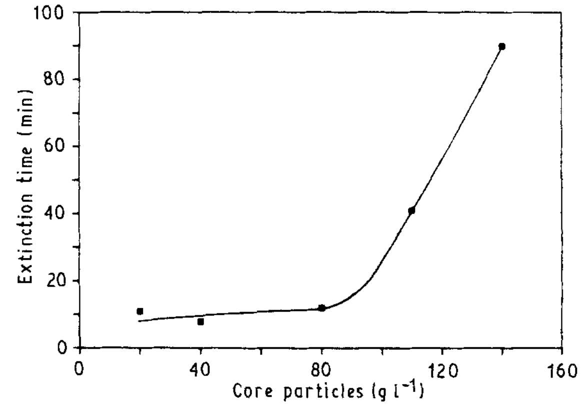

Figure 2 Plot of extinction time for silicon nitride particles catalysed in 50 cm^3 aqueous suspensions of (initial) pH 3, containing various amounts of the core particles, 0.2 g l^{-1} palladium chloride, 0.1 cm^3 30% ammonium hydroxide, and 0.4 g l^{-1} sodium hypophosphite, stirred at 45–50 °C for 15 min.

3.1.2. Treatment with Pd–Sn catalyst

The powder treated with the Pd–Sn catalysis process were successfully coated with electroless copper. The catalytic activity of the powders, inferred from the longer extinction time, was very poor when only 60 cm^3 37% hydrochloric acid was added per litre of the suspension. A sol of the untreated particles in deionized water was found to be alkaline in nature. The alkaline substance in the powders neutralized a part of the added hydrochloric acid. The catalytic activity was found to be greatly increased when more acid was added to reach a pH value corresponding to an acid solution of 60 cm^3 37% hydrochloric acid per litre in deionized water. Although systematic investigation of the effect of various experimental parameters such as palladium chloride and stannous chloride concentrations, temperature, and concentration of the core particles, was not carried out, the dramatic effect of pH on the efficiency of the catalysis process was evident.

It was shown earlier [12] that macroscopic surfaces, when catalysed by immersing in a Pd–Sn hydrosol, should be first washed with dilute hydrochloric acid. If the first rinse was done in water, the surfaces became passivated by a very thin layer of stannous hydroxide formed by the hydrolysis of stannous chloride present in the catalyst bath as a stabilizer. Treatment of the surfaces with acidic fluoride solution removes the passivating layer. Similar observations were made on the catalysis of submicrometre silicon carbide by the *in situ* reduction of palladium chloride with stannous chloride. The catalytic activity of the surface-treated powders was very poor when the first washing was done using deionized water. The powders were successfully coated with copper when the solids were first washed using 0.1 M hydrochloric acid.

TABLE I Extinction time for $PdCl_2/Si_3N_4$ ratio = 5×10^{-3} for particles catalysed in 50 cm^3 aqueous suspensions of initial pH 3, containing various concentrations of the core particles and palladium chloride, 0.1 cm 30% ammonium hydroxide, and 0.4 g l^{-1} sodium hypophosphite, stirred at 450–50 °C for 15 min. The copper coating bath contained 27 g l^{-1} core particles

No.	Palladium chloride concentration (g l^{-1})	Silicon nitride concentration (g l^{-1})	Extinction time (min)
1	0.1	20	23
2	0.2	40	8

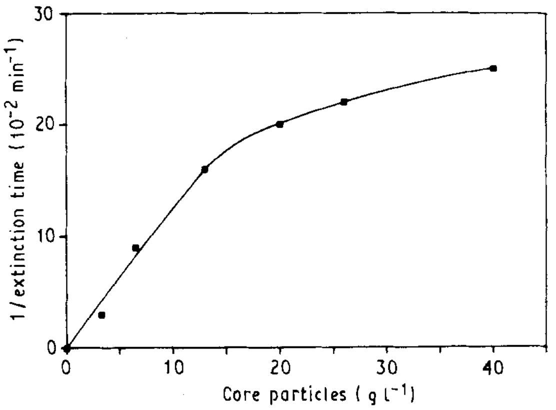

Figure 3 Dependence of extinction time on the silicon nitride concentration in electroless solution during micro-encapsulation with copper. The catalysis was carried out by stirring at 45 °C for 15 min, 1 litre aqueous suspension at pH 3, containing 40 g core particles, 0.2 g $PdCl_2$, 2 cm^3 30% NH_4OH and 0.4 g l^{-1} sodium hypophosphite.

3.2 Microencapsulation with nickel

After addition of the catalysed silicon nitride core particles to the green electroless nickel solution at 75 °C, the suspension turned black in ≈ 45 s. After 1 min, the dispersion was quenched by placing the

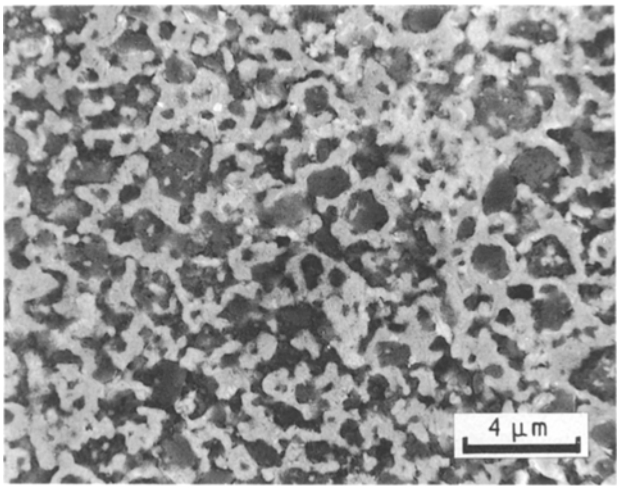

Figure 4 Scanning electron micrograph of the 72% Cu–28% SiC composite. The copper-coated SiC powders were uniaxially cold pressed at 51 MPa (7500 p.s.i.) and cold isostatically cold pressed at 680 MPa (100 000 p.s.i.).

TABLE II Extinction time for various types of core particles

Particle content no.	Particle type	Amount in copper bath (g l^{-1})	Extinction time (min)
1. Silicon carbide	Superior Graphite, USA	13	4
2. SiC whisker	American Matrix Inc, USA	13	90
3. Si_3N_4	UBE Industries (America) Inc.	13	8
4. SiC platelets	American Matrix Inc., USA	26	70
5. Titania	MCB Reagents, USA	13	22
6. Alumina	Alcoa, USA	13	3
7. Polymer particles	Darvan 820, W. R. Grace & Co., USA	6	7

reaction vessel in cold water and the solids were allowed to settle. The supernatant showed a weaker green colour than the fresh electroless nickel solution indicating that some nickel had been removed from the solution.

3.3. Consolidation of the powders

The density of the 72% Cu–28% SiC was 4.98 g cm^{-3}. The Vickers hardness of the composite was 120, which is nearly twice the measured hardness of fully dense, annealed 99.9% copper. Scanning electron microscopy revealed a uniform distribution of the silicon carbide particles in the copper matrix (Fig. 4).

4. Discussion

The extinction time, defined as the time required for the disappearance of the blue colour from the electroless copper coating solutions, was selected as the experimental index of the overall rate of disposition of copper. Visual blue colour detection, though somewhat subjective, was chosen because of obvious ease and simplicity of the method. The uncertainty in the measurements is estimated to be ≈ 30 s for the extinction time of 5–10 min, and 2–5 min for the extinction times of 60–90 min. Thus, the error in the measurement of extinction time was typically around 10%.

Considering the dependence on the concentrations of the palladium chloride (Fig. 1) and the core particles (Fig. 2), the extinction time might be expected to be relatively invariant at fixed $PdCl_2/Si_3N_4$ ratio, theoretically corresponding to constant surface coverage of the core particles with palladium atoms. However, such a behaviour was not observed (Table I), indicating that the nature of the catalyst layer is affected by the actual concentrations of palladium chloride and core particles.

The suspension of the non-catalysed core particles in electroless copper solutions remained chemically stable for a few days. With the surface-treated powders, the extinction time was found to decrease continuously with increasing core particle concentration in the copper coating baths (Fig. 3). These observations provided the experimental evidence of the catalytic nature of the surface-treated core particles. The curve in Fig. 3 is almost linear at low core-particle concentrations. This indicates that the kinetics of copper deposition are surface-reaction controlled, because only a small extent of surface area is available for coating. When more surface area is made available by higher concentration of these core particles, the rate of copper deposition should become limited by diffusion of the reactants from the bulk of the solution. This can, indeed, be inferred from the decreasing slope of the curve in Fig. 3 at higher core-particle concentrations.

A suspension of the untreated silicon nitride solids in electroless nickel solution was stable for 2 h at 75 °C, while the suspension containing particles treated with palladium catalyst turned black in < 1 min under identical conditions. Thus, the suitability of the catalysis process, using sodium hypophosphite as a reducing agent, was demonstrated for electroless microencapsulation of the fine particles with nickel.

The hypophosphite reduction process is of practical importance for several reasons. This catalytic treatment is essentially single step. The resulting suspension, after pH adjustment, can be directly used for electroless copper deposition. Thus, the steps of particle washing and transfer between several baths are obviated. For industrial applications, the process may result in savings in the corresponding equipment and operating costs compared with the traditional multistep processes. However, the catalytic activity of the surface-treated core particles depends on the amount of palladium on their surface. (Fig. 1). Thus, a meaningful cost analysis should address optimization of the amount of palladium chloride added per unit weight of the powder catalysed.

The catalysis process involving stannous chloride was successful only when the reduction was carried out at sufficiently low pH. It was observed that additional acid was required for powders which consumed part of the acid owing to their alkaline nature. Therefore, the measured pH value of the system was concluded to be a more important factor than just the amount of acid to be added as prescribed in the original recipe for the synthesis of Pd–Sn hydrosol [11].

It was established earlier [13] that excess stannous chloride leads to loss of catalytic activity of the Pd–Sn catalyst hydrosol. Investigations on the effect of stannous chloride concentration on the catalytic activity of the particles treated with the Pd–Sn process may be expected to follow similar trends.

The copper-coated colloidal powders were extremely reactive towards atmospheric oxygen. The powders turned black in a few minutes after exposure to air. This affinity of the copper coatings towards oxygen is attributed to the high specific surface area of the ultrafine coated particles.

The catalysis procedure using sodium hypophosphite as a reducing agent was successfully extended to the catalysis of several shapes and sizes of ceramic powders, as well as for polymeric particles. The results indicate the versatility of the process for the treatment of wide range of core particles of varying morphology. In addition, the catalysis procedure is effective for successful electroless microencapsulation of non-metallic powders with both copper and nickel.

The catalysis experiments also indicate that universal optimum conditions do not exist for all kinds and morphologies of the core particles. In fact, under otherwise identical conditions, the effectiveness of the catalysis process varies significantly with the nature of geometry of the core particles (Table II). Therefore, for the surface treatment of a particular type of core particle, the appropriate content of core particles, and concentrations of palladium chloride and sodium hypophosphite in the catalysis suspension should be individually determined.

Although the investigation on powder catalysis was limited to the use of sodium hypophosphite and stannous chloride as reducing agents, substances such as hydrazine [14], dimethylamine borane [14], triethyl amine borane [14], sodium stannate [15], glucose [16, 17], aminosilanes and methanol [18, 19], aminoacids and methanol [20], ascorbic acid [21], and mixtures of amino-sugars, methanol and butyl amine [22, 23], are potential candidates for the reduction of palladium chloride for the catalysis of the non-metallic powders. The use of these reducing agents in suspensions of core particles containing palladium chloride should be investigated to prepare powders of successful electroless micro-encapsulation with copper or nickel.

5. Conclusion

A one-step process, constituting the reduction of palladium chloride by sodium hypophosphite, was developed for the preparation of aqueous suspensions of activated non-metallic particles which could be directly used for electroless microencapsulation with copper or nickel. For this process, the catalytic activity of the surface-treated powders was found to be strongly influenced by several experimental parameters such as the pH, concentrations of the reactants, and the nature and amount of the core particles in suspension. Several kinds of non-metallic core particles of varying morphologies were successfully catalysed and coated with electroless copper. Consolidation of the copper-coated silicon nitride powders yielded a composite having a uniform distribution of the ceramic particles.

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