Progress in Deposition of Wear and Corrosion-Resistant Composite Alloys

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Silicon carbide particles co-deposited in a matrix of electroless nickel have been examined by SEM as part of a program to improve process control for reproducible wear-resistant coatings. Evidence suggests a possible contact transfer mechanism where SiC particles suspended in the bath strike the growing matrix and transfer a small amount of metal to sites on the SiC surface. Metal-to-metal friction forces between the sites and the growing matrix may contribute to particle attachment. The micro-transfer sites are revealed because they nucleate growth of micro-nodules of Ni-P on the SiC particles while they are suspended in the stirred bath, which also partially pre-coats particles. Observed features may add to the understanding of mechanisms by which micron-sized solid particles suspended in the plating bath become attached to and totally encapsulated by the growing deposited matrix metal. The interaction of partially pre-coated SiC particles with convective and diffusive mass transport in the boundary layer close to the electrode is also considered.

Keywords: *Wear-resistance, corrosion resistance, electroless nickel composites, SiC particles, mass transport*

Introduction

In composite plating, small solid particles suspended in the plating bath are co-deposited within a growing plated metal matrix. The particles are typically ceramic, although metals and polymers can also be co-deposited. The plating method can be electrolytic or electroless. For platers accustomed to well-filtered clean solutions, the purposeful addition of particles to the plating bath seems to be contrary to good practice. However, the incorporation of particles in composites brings about useful modifications of material properties. As interest in plating as a means to produce composite alloy coatings has grown, many new combinations and applications have been reported. At present, the mechanism by which particles become attached and totally encapsulated in the growing matrix is not well understood.

The present study concerns findings on mass transport effects related to the incorporation of silicon carbide particles in Ni-P. Many of the early theories about the forces which contribute to particle incorporation have focused on the electrical double layer and adsorption onto the surface of small-sized particles, typically less than 0.1 μm. For large particles mixed into the highly conducting concentrated solutions of practical plating, convection-diffusion forces just at the electrode surface must also play a role in addition to the double layer and electrophoretic effects more usually associated with small particles and dilute ionic solutions. Extending the size spectrum, we have examined the co-deposition behavior of SiC particles with major dimensions of 20 to 30 μm which require stirring to obtain suspension in solution. No additives such as surfactant wetting agents were used. We report some preliminary observations which broaden the picture of co-deposition. The present contact transfer results are limited to SiC/Ni-P but indicate a new path for consideration in furthering understanding of co-deposition mechanisms.

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Background

A few plated composites are already well-established industrial materials. Diamonds are co-deposited in nickel on the cutting edge of abrasive wheels used for dicing silicon wafers in the semiconductor industry. Co-deposited PTFE (Teflon) provides a self-lubricating low friction coating. Co-deposition of diamond and PTFE is reviewed by Riedel[1] and Feldstein.[2] Work on plated composites before 1995 has been critically reviewed by Hovestad and Janssen.[3]

In the rapidly growing literature on plated composites, recent reports (to cite but a few) discuss zinc with zirconia particles,[4] talc in nickel and Ni-P as a high temperature lubricant[5] and co-deposition as a method for the manufacture of sputter targets.[6]

Co-deposition is not limited to cathodic deposition but also occurs for anodic reactions. Casellato, *et al*.[7] have incorporated nanoparticles of titanium oxide and aluminum oxide in anodically grown lead dioxide. Electrically conducting particles may also be incorporated in a growing metal matrix, as reported by Parker[8] for various metal powders and by Donakowski, *et al*.[9] for graphite in zinc.

Theories about the mechanisms of composite plating have been proposed, notably by Guglielmi.[10] Modifications have been suggested by subsequent workers attempting to link particle density in the plated matrix with solution parameters. The modifications proposed by various authors are discussed by Hovestad and Janssen[3] who also comment on conflicting experimental results for different studies of the same system. However, key questions about the mechanism of particle co-deposition that still need attention are "How does a particle become initially attached to the growing matrix?" and "How does encapsulating growth proceed on the captured particle?"

Earlier theories based on modifications of Guglielmi's approach have concentrated on adsorption and electrophoretic effects to account for particle mobility and have excluded mass transport parameters which must, however, exert an influence close to the growing electrode surface.

It should be noted that the term "co-deposition" applied to solid particles is not entirely accurate from an electrochemical viewpoint, since Faraday's law is properly applied to electron exchange for reduction or oxidation of ionized species in solution. For example, alloys are co-deposited by simultaneous cathodic reduction of dissolved ions of the alloy components. However, any theories relating percent encapsulation with electrochemical and solution parameters should also consider that uncharged particles with sizes on the order of 20 to 30 μm can influence the flow of electrolyte in the mass transport boundary layer and thus can change the dynamics of plating at the surface.

In general terms, a particle suspended in the plating bath can approach the cathode closely by being carried along in convective flow past the electrode. A particle may make multiple contacts with the cathode but, in some manner, slows sufficiently to become trapped, perhaps by contacting slight irregularities in the growing metal surface. Once a particle is stationary, metal deposition can proceed to surround the particle at its perimeter and then grow laterally to complete the encapsulation. It may be expected that the first attached particles can cause a change in the local flow pattern, adding to the complexity of mass transport to and along the electrode.

The actual mechanism of attachment of a particle to the growing matrix is also without doubt complex. For example, a particle of insulating material can block current and affect the local current distribution just at the electrode during capture and subsequent encapsulation. Also, the presence of solid particles in the electrolyte can influence the fluid flow at the electrode surface by increasing the local viscosity. The trajectory of flat particles can be influenced by the velocity gradient perpendicular to the electrode surface. Accordingly, one might rightly suspect that fluid flow (and particle entrapment) at the electrode may be influenced by particle size and shape and volume concentration as well as by stirring rate. Our present findings for electroless nickel and silicon carbide composite focus attention on the possibility of frictional contact as a means by which small amounts of matrix metal are added to a particle, and which also assist the formation of a metal-to-metal bond which pins the particle to the surface.

For the present study, plating was done in a simple beaker cell with magnetic stirring to provide some definition of mass transport and to ensure suspension of particles. Smooth substrates were used for a preliminary evaluation of the effect of surface finish on the first stages of co-deposition. Other parameters examined include the concentration of particles suspended in the stirred solution and the volume fraction of SiC particles encapsulated in the grown matrix. For completeness, particles recovered from SiC residue in the cell after plating were also examined by SEM-EDS. Magnified views of SiC particles retrieved from the bath have provided new insights to the mechanism and complexity of composite plating.

Experimental

Features of co-deposition of silicon carbide particles in electroless nickel have been examined by scanning electron microscopy (SEM) (Hitachi 2400) and energy dispersive x-ray spectroscopy (EDS) for elemental analysis (EDAX DX-4). Deposits on a substrate were examined as well as SiC particles from particle sediment that settled after stirring ceased.

Separate experiments verified that (1) SiC by itself is not a catalyst for electroless nickel and (2) contact of stirred SiC particles with a solid surface transfers small amounts of the surface material to the particles. These experiments are described in more detail in Results and Discussion.

A smooth underlayer of electroless nickel provides a convenient initial substrate surface for examining the early stages of co-deposition. One such smooth substrate was formed by pre-plating Ni-P on a polished silicon substrate which was first activated by a sputtered thin film nickel seed layer to initiate smooth electroless deposition of Ni-P.[11] The smooth substrate was plated to a thickness of 19 μm in a high-phosphorus electroless nickel bath. Rigid memory disks (95 mm O.D.) with a plated and polished electroless nickel layer (12 μm, 12% P) plus a top layer of 300 Å of electroless cobalt (4% P) also served as a relatively smooth initial surface. Disk substrates with as-plated electroless nickel (12% P on 5586 aluminum alloy) were also used to provide a convenient initial surface with a definable roughness.

Plating was continued on the prepared substrates after adding SiC particles to the bath. SiC concentrations typically ranged from 1 to 10 g/L.

To provide definition of mass transport conditions, all plating was done in the same cell geometry, a one-liter Pyrex beaker seated on a magnetic stirrer hot plate. A flat circular cross-head type of Teflon coated magnetic stir bar (30 mm diam.) was rotated in the range 200 to 300 RPM. Stirring from rotation of a magnetic stir bar at the bottom of the cell kept some but not all of the SiC in suspension. At 300 RPM, one-fourth of the added SiC was in suspension. The rotational speed of the stirrer was determined in water with the aid of a laser RPM counter, but should be considered only as a rough estimate of the rotation of liquid coupled to the magnetic stir bar. All plated surfaces were positioned vertically in the bath. Ni-P plating temperatures were in the range 88 to 92°C, as measured with a glass-shielded chromel-alumel thermocouple immersed in the bath.

Silicon carbide used for all experiments was Fujimi Type GC600, a mixture of equiaxed (α crystal type) grains, 20 to 25 μm in diameter and flat flakes nominally 30 to 40 μm in a major dimension and approximately 2 to 10 μm thick, as determined from SEM photos. The particles are thus much larger than those reported in several studies of SiC co-deposition.

To determine the actual concentration of SiC particles suspended in the bath, small samples were siphoned from the bath into a graduated cylinder, allowed to settle and then decanted, washed and decanted again, dried and weighed.

The volume fraction of encapsulated SiC was estimated by quantitative counting of the area fraction of SiC particles in randomly selected directions on SEM photos. The fundamental basis of this simple and useful method is described by Underwood.[12] Typically, the volume fraction of silicon carbide in electroless nickel (mid-phosphorus) was about 25% for a 25 μm (0.001 in.) plated deposit (300 RPM stirring, 7 g/L SiC).

Results and discussion

Micro-nodules and craters are two notable features found on electroless composite deposition onto a smooth pre-plated Ni-P substrate from a high-phosphorus Ni-P bath with 9.7 g/L SiC. Many SiC particles are decorated with Ni-P micro-nodules, mostly at particle edges. As shown in Fig. 1 (1500×), micro-nodules are located on SiC particles which are already attached to the substrate surface. The presence of micro-nodules attached to SiC particles was an unexpected result, since SiC is not known as a catalyst for electroless nickel deposition. As mentioned above (Experimental), a separate experiment confirmed that SiC did not catalyze Ni-P under the same plating conditions when a substrate surface was absent from the stirred bath. The experiment is described in more detail in this section.

Craters, scratch markings and indentations on the surface are features not present on the initial smooth Ni-P surface. On the plated area, for example, a major scratch is the linear groove at the left side of Fig. 1. Smaller sharp-edged crater indentations are also at the right side of Fig. 1 and also below the major scratch on the left. Many craters have a V-shape and a tapered depth, a form that suggests a plowing action caused by a point on a sharp-edged SiC particle as it contacts and digs into the surface.

Indentations may be considered as evidence that a particle can hit the surface with sufficient momentum to cause plastic deformation of the matrix and can then retain enough energy to bounce back into the stirred suspension. Any matrix material attached to a SiC particle can act as a seed for fresh Ni-P deposition if the particle returns to the stirred suspension in the bath. Particle-to-particle contact in the stirred suspension may also contribute to transfer of seed material.

A nodule-decorated particle can return to the matrix surface as stirring continues. The ability of a returning particle to become captured when it hits the surface may depend on the product of particle mass and the square of the particle velocity, *i.e.*, its momentum. A contacting particle should have sufficient force to press attached Ni-P nodules onto the surface to create a friction weld with the matrix. Since plastic deformation of the matrix is required at the initial (and subsequent) contact by a particle, the hardness and yield strength of the matrix material also enter into consideration. The shape and roughness of a co-deposited particle are features that may influence attachment. Sharp corners and edges typical of SiC particles may be preferred for plowing up matrix metal. The growing matrix is probably being cut continuously as hard SiC particles still suspended in the stirred bath impact the surface. Already attached SiC particles can also be forcefully contacted by moving suspended particles which could break them away from the surface. Suspended particles could also exert a scrubbing action to dislodge protruding stationary nodules attached to an already captured SiC particle. The fact that micro-nodules remain attached in spite of the contacts from suspended particles suggests they are firmly bonded to the host SiC particle.

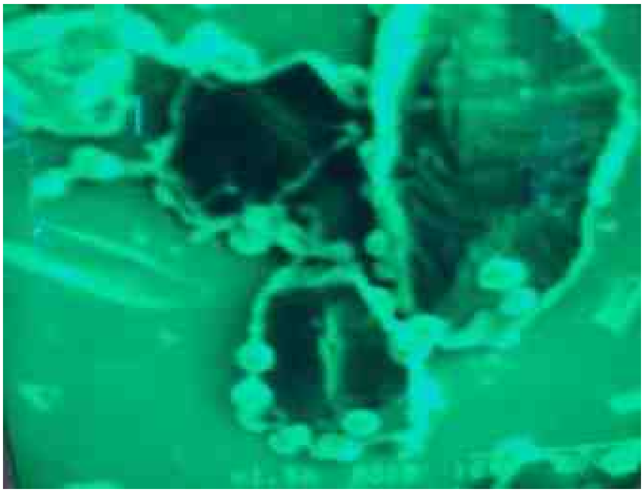

Figure 1 - SiC particles decorated with Ni-P micro-nodules; scratches in matrix Ni-P (high-phosphorus) (1500×).

Nodule growth on suspended particles suggests that a particle makes multiple contacts with the matrix during stirring and that only a fraction of such decorated particles become attached to the matrix. The rate of attachment to the growing matrix will determine the concentration of co-deposited particles in the resulting composite structure.

Another view of the as-plated surface is shown in Fig. 2 (2000×). Micro-nodules are located along particle edges and also on flat particle surfaces. A scratch with V-shaped depth profile is located in the smooth Ni-P region above the 20 μm marker bar.

The views in Figs. 1 and 2 are for an early stage of co-deposition since the thickness of the co-deposited layer is nominally only 5 μm, much smaller than the size of SiC particles. The thickness calculation was based on deposition rate determined from weight change measurements for the 19-micrometer Ni-P underlayer.

As mentioned, the micro-nodules attached to edges and surfaces of SiC particles (Figs. 1 and 2) are unexpected, since SiC is inert as a catalyst for Ni-P growth. Further, if SiC were a catalyst, complete coverage of the particle would be expected.

Without a metal surface available for suspended SiC particles to strike, there should be no contact transfer possible. To test the concept of contact transfer, SiC particles (7.7 g/L) were stirred in an electroless nickel (mid-phosphorus) bath in the absence of a solid substrate surface. Particles were thoroughly stirred in the bath for one hour at 93°C to duplicate the plating conditions associated with Figs. 1 and 2. Although there must have been particle-to-particle contact in the stirred SiC mass, in the absence of an immersed substrate surface, there was no micro-nodule generation and growth on the particles.

Figures 3 (600×) and 4 (1000×) show SiC particles after one hour at 93°C in a well-stirred mid-phosphorus Ni-P bath without an immersed substrate surface. The samples were taken from particle sediment that settled to the bottom of the cell when stirring was stopped. The sediment was air-dried but not washed in order to preserve as closely as possible the structure of particles as they were suspended in the stirred bath. There are no micro-nodules on the edges or faces of SiC particles. The few spots visible on particle surfaces are actually dried electrolyte, as determined by EDS elemental analysis. The test verified that SiC by itself does not catalytically initiate the growth of electroless nickel, consistent with results obtained in previous studies of alloys containing SiC.[13]

Figure 2 - SiC particles with Ni-P micro-nodules and scratches in the matrix Ni-P (high-phosphorus) (2000×).

If it is supposed that contact between substrate and particle is necessary for the transfer of a seed site to a SiC particle, then evidence of transfer should be visible on particles from the sediment in the cell after plating. A particle in the sediment may have contacted the substrate while it was suspended in the stirred solution but thereafter avoided capture by the surface. Figures 5 (800×) and 6 (2000×) show SiC particles from the sediment settled to the bottom of the cell after three hours of stirred plating onto a substrate similar to the initially smooth surface described for Figs. 1 and 2. The bath was high-phosphorus electroless nickel with a total SiC concentration of 8.2 g/L.

As shown in Figs. 5 and 6, micro-nodules of Ni-P are indeed attached to some SiC particles in the sediment remaining after plating. Micro-nodules of Ni-P are noticeably arrayed on particle edges. This could be the result of multiple contacts with the substrate or with already decorated particles in suspension.

Each of the two prominent edges of the large particle in Fig. 6 has Ni-P features where nodules appear to have grown and merged. Such growth could have occurred while the particle was suspended in the bath or while residing in the sediment at the bottom of the cell, since stirring does not completely suspend the entire amount of SiC added to the bath.

The presence of Ni-P micro-nodules on edges and surfaces of SiC particles may be interpreted in terms of contact transfer of traces of metal originating at first from the substrate and then from the growing Ni-P matrix. Contact

Figure 3 - SiC particles stirred 1 hr in a mid-phosphorus Ni-P bath, 93°C; no micro-nodules (600×).

Figure 4 - SiC particles stirred 1 hr in a mid-phosphorus Ni-P bath, 93°C; no micro-nodules (1000×).

transfer may occur generally during co-deposition of hard ceramic particles with other metal substrates. However, in the case of electroless deposition, the contact site is revealed because of nodule growth catalyzed by the transferred trace of Ni-P. Verification of contact transfer as a general effect of importance in co-deposition awaits additional experimentation, especially for smaller SiC particle sizes and for other ceramic particles and matrix metal combinations.

As a start in accounting for micro-nodules, we know the SiC does not nucleate growth by itself. Since micro-nodules are positioned mostly at particle edges, we may reasonably suspect contact between particles and a solid catalytic surface to be a necessary step for transfer of catalytic Ni-P to the SiC particle. A two-step experiment gave additional information about contact transfer to sites which grow into micro-nodules. The transfer sequence was divided into two experimental steps - first, solid to particle contact in a stirred suspension without plating followed by a second step of plating to permit growth.

In the first step, the beaker cell contained a solid surface immersed in a mixture of 500 mL of deionized water at 25°C plus SiC particles at a concentration of 1.3 g/L. The solid surface was a 100-millimeter diameter Ni-P plated and polished rigid memory disk. The water-SiC particle mixture was stirred at 300 RPM for four hours with particles contacting both sides the immersed disk. After the contact time, the disk was removed and the water drained nearly completely from the beaker. A small sample of the SiC residue was taken, washed and dried for subsequent SEM examination. For the second step, the wet SiC residue in the beaker was quickly covered by 300 mL of mid-phosphorus electroless solution, and then stirred at 300 RPM for two hours at 90°C. SEM showed the presence of Ni-P micro-nodules on SiC particles in a sample taken from the 90°C second step. Remarkably, Ni-P sites attached to SiC from the first step at 25°C were not detectable by SEM-EDS, although sharp edges of several particles were probed, searching for a signal from a site with high-phosphorus composition. First-step (water, 25°C, Ni-P solid surface) particles had the exact same appearance as SiC particles stirred in a 90°C Ni-P bath without an immersed catalytic surface (Figs. 3 and 4). However, micro-nodules are indeed visible on particles after the second step (2 hr, 90°C mid-phosphorus bath) which provided an opportunity for contact transfer sites (Ni-P, water, 25°C) to develop, as shown in Fig. 7. Micro-nodules grown in the second step had the expected mid-phosphorus composition of 8% P.

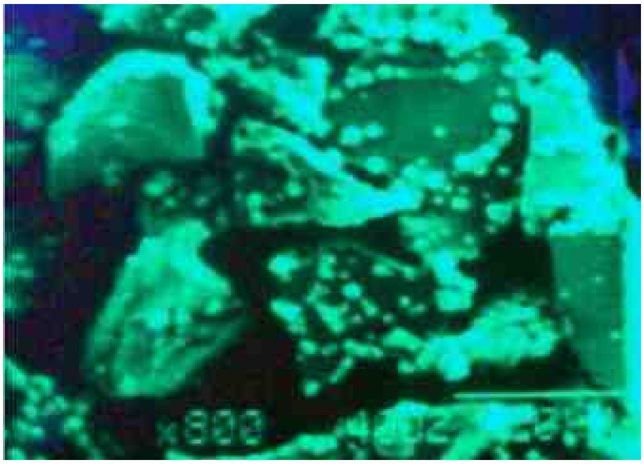

Figure 5 - Sediment after 3 hr Ni-P (high-phosphorus) plating, 8.2 g/L SiC (800×).

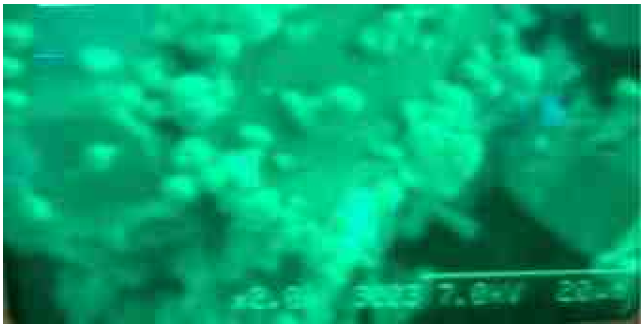

Figure 6 - Sediment after 3 hr Ni-P (high-phosphorus) plating, 8.2 g/L SiC (2000×).

In the two-step experiment, the disk surface is the likely source of extremely small sites that transfer to SiC particles. In continuing experimentation, scratches and craters produced on smooth and textured substrates by SiC (and other particles) will be examined in an effort to relate surface features with particle size and concentration, stirring rate, time of contact and also mechanical properties of the substrate surface.

The two-step contact-growth experiment strongly suggests that very small amounts of Ni-P are transferred from a substrate to SiC particles when the stirred particles strike the solid substrate. An alternative concept of activation of otherwise inert SiC as a result of impact with a solid surface is less likely.

Figure 7 - Nodules grown at 90°C, mid-phosphorus on SiC particles first stirred in contact with Ni-P surface in water, 25°C (1500×).

To tie together nodules and scratches, consider that stirring brings particles into contact with the substrate with sufficient force to scrape the surface and transfer a small amount of substrate material to the SiC particle, particularly at a sharp edge. The transfer of microgram amounts of material during adhesive wear and frictional sliding contact between metals is well-documented.[14] From radiotracer and chemical measurement techniques, transferred material between lubricated surfaces has been estimated to have minimum layer thicknesses of about 20 Å, entirely adequate for initiation of Ni-P deposition by a catalytic material. Such friction contact areas are also believed to be rough because of plastic deformation as contact bonds are broken. The particle may become attached to the substrate during a subsequent contact or may continue to hit and bounce back into the stirred suspension, but once the trace of metal is attached, it can act as a seed to promote additional growth while the particle is circulating in the stirred bath.

For particles that bounce back into suspension with edges decorated with small contact transferred Ni-P sites, the probability of capture of such particles at a later contact with the surface may be increased by the number and size of micro-spheres attached to the surface. The average density of a suspended SiC particle must increase as its added load of micro-spheres continues to grow by virtue of electroless reaction. As mentioned, the mechanical hardness and plasticity of the substrate metal may also be a factor related to the ease of metal transfer upon impact. As a practical matter, control of plating bath composition should account for reactant depletion since nodules attached to decorated but uncaptured particles can continue to grow while still in suspension.

The instantaneous roughness of the growing (and initial) matrix surface must play a role in the dynamics of particle capture. A rough surface profile is available from already captured particles, from micro-spheres of Ni-P on particles and from scratches in the growing surface caused by fresh particle impacts. Any nodular Ni-P formation on the matrix as it grows can also contribute to surface roughening.

Several events that influence co-deposition must take place simultaneously in a busy zone immediately close to a growing matrix. Convective flow brings particles into the zone which strike the surface and pick up a small amount of transferred metal. Some of the same flow of particles may strike the surface without metal transfer. Particles with or without transferred metal may bounce back into the main volume of stirred suspension, ready to strike again. While particles continue to circulate, nodules can begin to grow on those with seed sites, thus changing the flow behavior of the suspension as well as the effective viscosity and velocity distribution close to the growing substrate. Particles with added nodule mass might also make deeper craters and scratches upon impact with the growing matrix.

Deposition of the matrix metal continues at the matrix side of the busy zone of particle motion. For electroless Ni-P, convective-diffusive mass transport brings fresh reactants from the electrolyte of the stirred suspension to support the deposition rate and also takes away ionic reaction products. To add to the overall complexity for Ni-P deposition, convection at the electrode is also supplemented by an upward solution flow resulting from evolution of hydrogen bubbles from the growing surface.

The physical and chemical processes that permit a SiC particle to become firmly attached to the matrix Ni-P are not obvious, especially in the presence of the surrounding solution. One possibility is that the mechanism of attachment is related to friction and metal-to-metal bonding equivalent to cold welding within an electrolyte. Contact transfer first requires adhesion of a small amount of the Ni-P matrix to a SiC particle. It is conjectured that locking of a SiC particle onto the matrix surface involves bonding between the Ni-P matrix and a Ni-P site already positioned on the edge of a SiC particle. The continual abrasion of the surface by suspended particles must clean the surface of any oxide which might tend to form. The same may be said for the metal transferred to particles by such contacts and also metal that has already grown into micro-nodules. In addition, all Ni-P surfaces in the electrolyte are sites of hydrogen evolution which may provide a form of cathodic cleaning. The key question is whether contact between clean surfaces can result in local metal-to-metal bonding strong enough to hold and lock a SiC particle in place for encapsulation by the growing matrix.

Support for friction-induced metal-to-metal bond formation is found in results drawn from the field of friction and wear (tribology). As mentioned, it is well known that traces of metal are transferred between sliding surfaces, an effect generally termed adhesive wear.[14] Metal-to-metal cold welding can also occur in a room temperature liquid environment. Friction between surfaces in electrolytes has been measured for contact motion of a few millimeters and, more recently, on a nanometer scale using variants of atomic force microscopy (AFM). However, all such electrolyte studies find conditions for stick-slip friction between metal and ceramic and also for metal-to-metal contacts. It is generally agreed that stick-slip friction indicates continual plastic deformation and formation of micro-welds at minute high spots (asperities) with continual breaking of welded micro-regions by shear forces as sliding proceeds. In other words, the fluctuating coefficient of friction of stick-slip behavior also implies cold welding and metal transfer between contacting surfaces in an electrolyte. Traces of metal are transferred in sliding friction even without stick-slip behavior.

The history of friction in electrolytes up to 1975 is noted by Dubois, *et al.*[15] who demonstrated that the potential applied to the metal can affect the coefficient of friction and result in metal-to-metal transfer. The friction coefficient between gold and silica (in 1N H_2SO_4), was a steady 0.15 at reducing potentials but rose at oxidizing potentials, oscillating from 0.6 to 0.8, indicating stick-slip behavior.

The findings of Dubois, *et al.* are in agreement with earlier work on friction of electrochemically polarized platinum, reported by Bowden and Tabor.[16] In recent AFM studies, Hausen, *et al.*[17] also find stick-slip friction of polarized metal surfaces in various electrolytes.

Frictional contact transfer may prove to be a general effect in particle-matrix co-deposition. Data for practical systems such as electroless nickel are not available. Direct measurement of bonding between the surface of the growing Ni-P matrix and Ni-P positioned at contact transfer sites on SiC particles poses an experimental challenge. At present, we can say only that the co-evolution of hydrogen suggests at least a partially clean surface at the mixed potential of the redox reactions of electroless Ni-P deposition.

For electroless Ni-P, the capture and attachment of a relatively large decorated SiC particle to the growing matrix may be an isolated special case of co-deposition. One might ask whether contact transfer is a general effect to be expected in other systems. The dynamics of particle capture and encapsulation may also include mechanical effects other than contact transfer. Yet to be determined is whether contact transfer or a related mechanism is involved in anodic co-deposition and in the co-deposition of polymers such as PTFE.

For electrolytic systems, traces of metal might also be added to hard particles by contact transfer even though not revealed by micro-nodule growth in suspension comparable to the case of Ni-P. Contact transfer sites may also assist particle capture and attachment. For example, metal-to-metal friction at site-to-matrix contact may help to slow or stop the motion of a suspended particle sliding along the matrix surface. A pre-capture build-up of growth on a suspended particle may require multiple contacts of an already partially metallized region with the cathode or by current flow from particle to particle with one of the partially metallized particles in momentary contact with the cathode, all taking place within a zone close to the growing matrix surface. Electrolytic pre-coating of particles may resemble barrel plating where deposition proceeds by contact between part and dangler and by part-to-part contact.

A common feature of all co-deposition systems is the ability to trap a moving particle on the surface. Any initial roughness above or below the average surface plane may serve to initiate particle trapping. Whatever type of mechanical bonding holds the particle in place on the surface, the following step of encapsulation is most likely controlled by electrochemical factors such as current density and the convective supply of reactant ions. Any new surface irregularities resulting from plating can further assist mechanical trapping as the co-deposition continues. Accordingly, the parameters that describe the dynamics of a co-deposition system (particle size, concentration, stirring rate) should also consider hardness of particle and substrate as well as a measure of initial surface roughness, changes in surface roughness profile as deposition proceeds, and the effect of solution parameters on the velocity and mass transport boundary layer thicknesses in the zone adjacent to the growing matrix.

Summary and conclusions

The existence of metal sites transferred as a result of sharp edges of hard SiC grains impacting a growing surface has been inferred because they amplify their presence by growing into micro-spheres. Growth proceeds by electroless deposition as the particles remain either suspended in the stirred bath or on particles already attached to the growing deposit. In principle, electroless nickel deposition can be triggered by a monolayer of catalyst material so that a small trace of metal transferred to SiC can grow out to form recognizable micro-spheres. Otherwise, the possibility of contact transfer would not be noticed. It should also be noted that the SiC particles of the present study are larger than SiC grain sizes used in most studies of co-deposition. They impact with more force which increases as suspended particles become heavier as attached micro-spheres grow.

As noted, the presence of Ni-P micro-nodules anywhere on the face or edge of a SiC particle is totally unexpected. A separate check experiment verified that stirring of a suspended mass of SiC particles by itself did not activate catalysis for Ni-P micro-nodule deposition. It was also shown that contact of suspended SiC particles with a solid catalytic surface results in micro-nodule growth.

The facts obtained from the behavior of the micro-nodules point to a new type of mechanism for attachment and encapsulation, at least for SiC co-deposited with Ni-P. A plausible sequence is suggested as follows:

1. Suspended SiC particles gain momentum in the electrolyte flowing past the matrix metal.
2. A particle turns in the velocity gradient close to cathode and contacts the surface of the matrix.
3. A small amount of metal is transferred to the SiC particle.
4. Contact with the matrix metal may occur several times for one particle.
5. Metal transferred to SiC particles that bounce back into suspension in an electroless bath continues to grow, becoming spherical nodules on the particle.
6. The matrix surface continues to grow, developing micro-scale surface irregularities which usually accompany electroless plating.
7. As a result of particle impacts on the surface and on micro-nodules at any stage of their growth, these surfaces are cleaned and a pre-coated particle may strike the matrix surface and form metal-to-metal bonds which assist anchoring of the particle to the surface.
8. Particle impacts can continuously scar the growing matrix surface, thus providing additional sites for slowing and trapping particles with protruding micro-nodules.
9. Any particles already trapped on the surface or being encapsulated can be barriers which slow new particles moving close to the surface.
10. Encapsulation growth is assisted by some pre-coating of particles by micro-spherical nodules while suspended in the bath.
11. The growth of matrix Ni-P metal and the attachment of Si-C particles may be considered as independent steps of the co-deposition process.

Some elements of the proposed sequence may be of general use in developing a better understanding of particle-matrix co-deposition.

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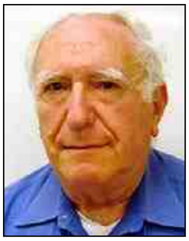
About the authors



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