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Selective Electrodeposition of Nanoparticulates into Metal Matrices

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ABSTRACT

Pulse-reverse electrodeposition has been used to co-deposit γ-Al_2O_3 nanometric size particles, $\leq$30 nm in diameter, into a copper matrix, from electrolytes where the particle diameters exceed 150 nm. The selectivity effect inherent to the pulse-reverse method is independent of the electrolyte convection and, additionally, results in a higher particle deposit concentration compared to direct current deposition. The technique provides a means to develop bulk nanocomposites with particle size distribution control.

Metal matrix nanocomposite thin films exhibit unique magnetic, mechanical, and optical properties and are promising materials for microdevices. The deposition of nanocomposites may also be of interest for fundamental studies of their nanometric nature. Electrodeposition offers a cost-effective means to fabricate them onto flat or irregular shaped surfaces. An insoluble, second-phase particle is suspended in a conventional plating electrolyte and is integrated into the growing metal film. The technique has been widely demonstrated for a variety of metal-particle systems where the *mean* particle size is in the nanometer to micron range and has been the subject of several reviews.[1−3] The engulfed particles are representative of those present in the electrolyte. Thus, variations in particle sizes, due to either processing or agglomeration effects, are reflected in the resulting deposit. For the first time, a pulse-reverse (PR) plating procedure is presented here, demonstrating that nanoparticles can be selectively co-deposited with the metal film even when a great disparity of particle sizes exists in the electrolyte. This eliminates the need for careful particle size control in the electrolyte and suggests a novel method for nanocomposite synthesis.

Podlaha and Landolt[4,5] have used the pulse-reverse technique with rotating cylinder electrodes to greatly enhance alumina particles into a copper matrix containing only 12.5 g/L γ-Al_2O_3. Typically, particle loading in the electrolyte is in the range of 10 to hundreds of grams per liter, since higher particle concentration in the electrolyte tends to yield higher amounts of particles in the deposit up to a limiting value.[6] Large particle electrolyte concentration is problematic because it promotes agglomeration and increases the difficulty to keep particles uniformly mixed and suspended in the solution. Since the pulse-reverse scheme can enhance the particle deposit concentration, fewer particles need to be present in the electrolyte. The PR method employs long, steady-state pulses several seconds to minutes long. The metal and particles are deposited during the cathodic cycle. During the anodic cycle, part of the metal is removed and thus concentrates the co-deposited particles. It was previously shown that the particle deposit concentration can be improved up to six times over that found with unmodulated, direct current (DC) electrodeposition.

Short pulses, on the order of milliseconds, have been employed by Kariapper and Foster[7] for composite plating. They reported no particle incorporation enhancement, but a loss of particle co-deposition if the pulse time length is too rapid. Pulse plating, without an anodic component, has also been reported by Chen and Sautter[8] with rapid pulses. A moderate increase in particle deposit concentration was noted, coupled with a change in the surface microstructure. No particle size selectivity has been previously noted.

The selectivity approach taken here requires that deposition and dissolution proceed uniformly over the electrode surface. The pulse-reverse method then captures particles that are of the same order or smaller than the net thickness of the deposit per cycle. The pulse deposition time scale should be sufficiently long so that particles can adhere to the growing metal surface during the cathodic cycle, as suggested by the results of Kariapper and Foster,[7] and to avoid nucleation surface nonuniformities in both the cathodic and anodic steps. During the cathodic deposition cycle, all particles of variable sizes are incorporated into the deposit. The anodic dissolution cycle is carried out to thin the deposit to the desired nanometer thickness, releasing particles that exceed this size. Electrolyte agitation ensures that the large particles are sheared away from the electrode surface as they are freed. The results presented here employ both a rotating disk and

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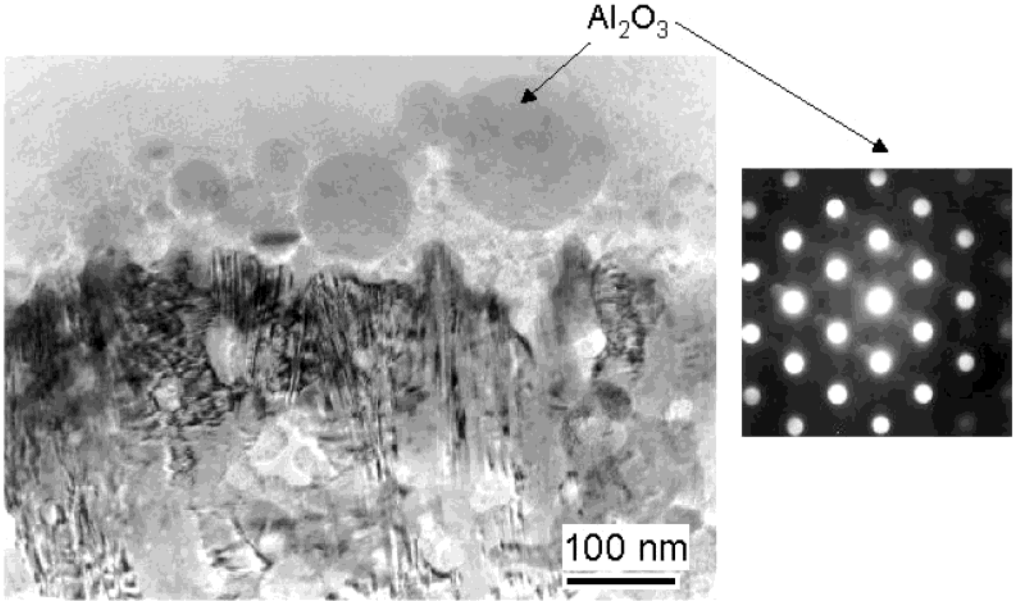

Figure 1. Bright-field, cross-sectional TEM image of a DC-plated composite on a rotating disk electrode with a wide particle size distribution. The electron diffraction pattern shows the [110] direction.

cylinder electrodes in order to simulate both laminar and turbulent flow environments demonstrating the generality of the technique. The copper$-\gamma$-Al_2O_3 system is chosen as a model system.

The nanocomposites were deposited onto rotating electrodes from a copper-citrate electrolyte containing 0.25 M $CuSO_4{\cdot}5H_2O$, 0.3 M $C_6H_5Na_3O_7{\cdot}2H_2O$ and 12.5 (or 25) g/L γ-alumina particles. The pH was set to 4.0, adjusted with concentrated sulfuric acid. The alumina particles were produced by the gas-phase condensation method and had an average particle size of 32 nm (lot #AM60220-01, Nanophase Technologies Corporation, IL). The deposition and dissolution current densities were -5 mA/cm^2 and $+10$ mA/cm^2, respectively.

The electrode material was 304 stainless steel plated with a 0.5 μm Au surface. The rotating disk diameter was 0.6 cm (surface area = 0.283 cm^2), and the rotation rate was 1600 rpm. The cylinder length was 1.2 cm, having a diameter of 1.0 cm (surface area = 3.77 cm^2). The cylinder was recessed 0.3 cm from the edge of the insulating shaft, and the rotation rate was 800 rpm. A copper foil, formed into a large stationary cylinder, was used as the counter electrode and placed concentric to the cathode. Pulse-reverse electrodeposition was carried out with a potentiostat/galvanostat interfaced with a pulse generator to provide the square wave pulses. The bulk alumina concentration was measured with an electron microprobe with a wavelength dispersive spectroscopy WDS detector. The microstructure near the electrode center was characterized with a high-resolution transmission electron microscope (TEM).

The choice of using the citrate electrolyte and the specified applied current densities was to promote a uniform deposition over the electrode surface. Copper electrodeposited from citrate electrolytes has been shown to exhibit sluggish reaction kinetic rates.[9] The applied current densities were chosen so that the metal deposition and dissolution were under kinetic control. Due to the geometry of the rotating disk electrode, a nonuniform current distribution may develop if the Wagner number (Wa) is much less than one.[10,11] The corresponding Wa at the conditions here were determined by $Wa = (\partial\eta/\partial i)/(L/\kappa)$, where $\partial\eta/\partial i$ is the change in overpotential with applied current density, κ, the solution conductivity, and L a characteristic length, taken as the disk radius. The slopes of both the anodic and cathodic polarization curves were measured from the two electrolytes, one containing 12.5 g/L γ-alumina particles and the other 25 g/L γ-alumina particles. The slopes were equivalent between the two electrolytes. The solution conductivity was measured (0.053 Ω^{-1} cm^{-1}), and the two Wagner numbers determined, $Wa_{\text{cathodic}} = 2.7$ and $Wa_{\text{anodic}} = 2.0$ for the deposition and dissolution conditions, respectively. These values suggest that for a disk electrode, a relatively uniform deposition and dissolution distribution ensues along 80% of the electrode surface, with a small rise in current density near the electrode edge.[11] For the rotating cylinder electrode, a recess has been added to the edge of the electrode that would promote a more uniform current distribution than that given by the disk.

Figure 1 shows a TEM composite cross-sectional DC electrodeposit on the rotating disk electrode, without current modulation. Particles of various diameters, ranging from tens to hundreds of nanometers, are incorporated into the deposit from the electrolyte containing a distribution of γ-Al_2O_3 particle sizes. The applied current was -5 mA/cm^2 with a deposition time of 2000 s and a total deposit thickness of 3.7 microns. The nanobeam electron diffraction pattern in Figure 1 reflects the crystalline structure of the large alumina particle present at the deposit surface.

The selectivity feature is observed in Figure 2a,b when the modulated pulse-reverse deposition is employed with the disk electrode. The cathodic applied current density remained the same with a deposition time of 120 s. The introduction

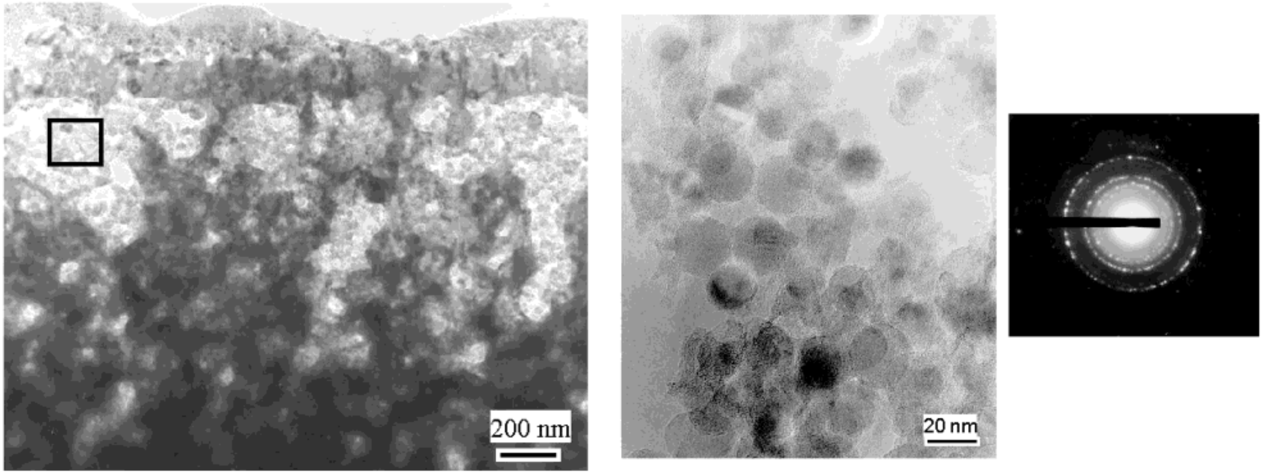

Figure 2. (a) Bright-field, cross-sectional TEM image of a nanocomposite electrodeposited with the PR method onto a rotating disk electrode showing the absence of particles greater than 100 nm. (b) High magnification of the boxed area in (a). The electron diffraction pattern reveals nanometric particles less than 30 nm incorporated into the deposit.

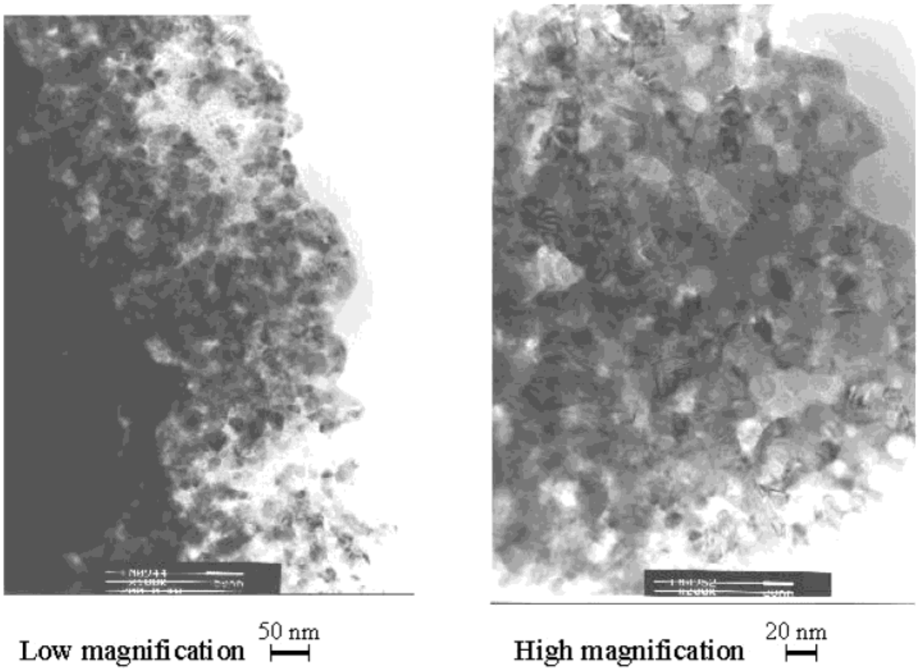

Figure 3. Low and high magnification cross-sectional TEM images of a nanocomposite electrodeposited with the PR method on a rotating cylinder electrode.

of the anodic step at 10 mA/cm^2 for 48 s corresponded to a duty cycle of 0.2. The bulk material is a result of 83 cycles, chosen to maintain the same net deposition charge as in the DC deposit. Figure 2a shows, under low magnification, that the larger particles on the order of 100 nm are not present. Figure 2b is a high resolution image that clearly shows the incorporation of particles below 30 nm and the absence of larger ones. The selected area electron diffraction over the enclosed region in Figure 2a shows the randomly oriented pattern of the collection of nanometric particles.

To demonstrate the generality of the technique, the pulse-reverse electroplating method was also carried out on rotating cylinder electrodes with an electrolyte containing 25 g/L γ-Al_2O_3. Figure 3 shows a low- and high-resolution TEM micrograph for a pulse-reverse plated deposit with the same deposition conditions. The low magnification is to verify the absence of the larger particles, and the high magnification shows the selective incorporation of the nanometric size particles.

In addition, there is an enhancement of particle deposit concentration when pulse-reverse (PR) plating is employed compared to direct current (DC) plating. Table 1 lists the particle deposit content for the different plating environments. The variation in wt % alumina listed in Table 1 represents the average standard deviation of the alumina concentration over the electrode surface. The reproducibility of the average particle concentration was between 0.1 and 0.3 wt % alumina for the DC deposits. Greater compositional fluctuations were found for the PR deposits, and the average particle concentration varied between 1 and 2 wt % alumina.

Table 1: Alumina Deposit Concentration

electrode configuration	particle electrolyte concentration, g/L	wt % alumina	
		DC	PR
cylinder electrode, 800 rpm	25 (this study)	7.5 ± 2.2	12.7 ± 2.9
	12.5 (ref 4,5)	3.5 ± 0.7	14.6 ± 1.1
disk electrode, 1600 rpm	12.5 (this study)	2.9 ± 0.2	6.8 ± 0.4

The pulse-reverse method that has been developed here is useful to selectively incorporate nanometric size particles into a metal matrix. The size of the captured particle is the same size as or smaller than the net deposit thickness in one cathodic/anodic cycle, which can be easily controlled by the applied charge. An added benefit is that the method can be used to augment the deposit particle composition. The usefulness of this technique is not only to narrow the particle size distribution in composite materials but also as a separation method in the nanometer range.

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