Electroplating Nanocomposite Films with an Impinging Jet Electrode

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An impinging jet system was used for electrocodeposition of nanocomposites utilizing significantly faster deposition rates when compared to conventional methods. An acidic copper bath with various loadings of 50 nm γ -alumina and 1 μ m α -alumina particles was used to produce nanocomposites with particle incorporations ranging from 0.5 to 7.0 wt%. The process variables affecting particle incorporation were current density up to 200 mA/cm², electrolyte flow rate up to 8.0 L/min, and particle loading from 30 to 120 g/L. Electrogravimetric measurements gave particle incorporation results with a reproducibility of ±0.2 wt%.

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Introduction & Background

Metal matrix composite films can be made by the process of particle incorporation during the electrolytic deposition of metal. Composite coatings produced in this manner have successfully incorporated particles of pure metals, ceramics, and organic materials ranging in size from 1 nm to 100 μ m (3.94x10⁻⁸ to 3.9x10⁻³ in.) in diameter into Cu, Ni, Co, Cr, and various alloys. The concentration of particles suspended in solution (particle loading) has varied from 2 to 200 g/L (0.016-1.6 lb/gal), typically producing composites with 1-10 vol% embedded particles.¹⁻⁵ When gravity settling was used, incorporations up to 50 vol% have been obtained.⁶ Nanocomposite coating has been previously studied using electrocodeposition with a rotating cylinder electrode system.^{7,8}

Electrocodeposition plays an important role in many technological areas. Specific applications include surface coatings for cutting tools,⁹ dispersion strengthening of materials with high thermal conductivities for use in actively-cooled structures,¹⁰ high surface area electrodes for electrocatalysis in solar energy conversion and hazardous waste treatment,¹¹ lubrication of surfaces,¹² and wear resistance in aircraft engines.¹³ Advantages of composite electrodeposition over other coating methods include the following: uniformity of deposition, even for complex shapes; reduced waste, especially as compared to dipping or spraying techniques; low levels of contamination; and ability to continuously process parts. In addition, this process avoids the problems associated with high temperature and high pressure processing. Most of the work concerning electrocodeposition has focused on maximizing particle content or improving a specific property of the codeposited film, such as corrosion or wear resistance.

Electroplated composite coatings have been found to exhibit inhibited grain growth, higher hardness, reduced wear and corrosion, and higher flow stress.¹⁴⁻¹⁷ Bulk nanocomposite materials formed by ball milling of copper powders with nanosized alumina particles had grain refinement to 1 μ m, leading to increased hardness and yield stress.^{17,18} Copper reinforced with alumina nanoparticles also can maintain good electrical conductivity while exhibiting excellent thermal stability.¹⁹

Reviews of electrocodeposition have been written by Greco¹, Hovestad and Janssen,²⁰ and recently by Stojak, Fransear and Talbot.²¹ From the research on electrocodeposition to date, a number of variables appear to be influential in the process, including hydrodynamics, current density, particle characteristics, bath composition, and particle-bath interactions. The influence of a particular variable on the process is typically assessed from the magnitude of the change in particle incorporation obtained when that variable is adjusted.

Impinging jet electroplating has been utilized for the plating of copper, gold, and nickel.²²⁻ ²⁴ Plating has been accomplished in both submerged and unsubmerged jet plating systems. Deposition rates for jet plating have been reported²⁵ to be up to 10 times greater than those of conventional plating methods, with current densities as high as 4 A/cm² (25.8 A/in²) A mass transfer correlation for limiting current density has been found for an unsubmerged impinging jet electrode (IJE).²⁶ In this correlation, the nozzle to substrate gap, flowrate, and nozzle diameter are variables used to determine limiting current density. Previous studies of electrodeposition with an IJE have primarily focused on maskless lithography.^{22,23,27} Placing the nozzle close to the substrate hydrodynamically limits the area of deposition to a width proportional to the inner nozzle diameter, allowing for selective or localized metal deposition. The impinging jet greatly enhances deposition rates because convection leads to high rates of mass transfer.²⁸ Typically, deposits are evaluated by comparing their width to the inner nozzle diameter and their thickness to the deposition time. There has been little work to evaluate IJE plating as a method of producing bulk or composite films.

Recently, electrocodeposition with an unsubmerged IJE has produced incorporations of up to 30 vol% SiC in a nickel matrix.²⁹ For the IJE configuration, composites of Ni-Al₂O₃³⁰ and compositionally-graded Ni-P deposits containing SiC particles²⁹ have been obtained. However, no systematic research has been done to characterize the effects of hydrodynamics on particle incorporation with an IJE. The objective of our research has been to develop an unsubmerged IJE system to investigate the electrocodeposition of nanocomposites of alumina particles in copper and to compare our results with our previous studies using a rotating cylinder electrode.³⁰

Experimental Apparatus & Procedures

An IJE system was developed for the electrocodeposition of metal matrix composite films, as shown in Fig. 2. In this system, the electroplating cell was suspended directly over the 8 L (2.1 gal) solution tank. This allowed for continuous recycling of the electroplating slurry bath without particle buildup in the electroplating cell. A 1.2 cm (0.47 in.) diameter copper pipe approximately 40 cm (15.7 in.) long served as a soluble anode and nozzle. An electric diaphragm pump with an 8 L/min (2.1 gal/min) capacity was used to circulate the electroplating slurry. The flow rate was adjusted with a pair of ball valves that regulate flow through the main and bypass streams. Flow rate was measured with a digital paddle wheel flow meter. The substrate was suspended below the nozzle from the top of the electroplating cell by two acrylic tubes. The substrates for this experiment were 2 cm (0.79 in.) squares of 0.13 mm thick (5.1×10^{-3} in.) copper foil. Electroplater's tape was used to fix the substrate to the electrical connection and mask the deposition area (0.8 cm² or 0.12 in²) by cutting a 1 cm (0.39 in.) diameter hole into the tape. Particle suspension was maintained with a laboratory stirrer with a paddle impeller. A galvanostat/potentiostat controlled the current applied in the system and its coulometer measured the charge passed during deposition.



Figure 1 - Impinging jet electrode system

The copper plating solution was 1.0M CuSO₄ and 1.2M H₂SO₄. Electrocodeposition experiments were conducted at room temperature using either 50 nm (~2x10⁻⁶ in.) γ -Al₂O₃ or 1µm (~4x10⁻⁵ in.) α -Al₂O₃ particles with loadings of 20, 40, 80, and 120 g/L (0.16, 0.39, 0.49, and 0.99 lb/gal). Experiments were conducted galvanostatically with current densities from 25 to 200 mA/cm² (3.9 - 31 mA/in²) and flowrates from 0.5 to 7.0 L/min (0.13 to 1.8 gal/min). The nozzle was set at 6.5 mm (0.26 in) above the substrate. Particle incorporation was determined by electrogravimetric analysis. For electrogravimetric analysis, charge measured by the coulometer is used to calculate the mass of the copper deposited. Particle incorporation is then calculated from the difference between the actual sample mass and the copper mass determined from coulometry. The typical weight of a codeposited film was 0.1 g (2.2x10⁻⁴ lb), resulting in an accuracy of ±0.2 wt% for particle incorporation. The corresponding film thickness was approximately 30 µm (1.18x10⁻³ in.). The reproducibility of incorporation for at least three depositions was approximately ±0.2 wt%. Particle distribution was determined by scanning electron microscopy (SEM) analysis of the substrate side of the deposit. Surface morphology of the deposited surfaces was also analyzed with SEM.

Results & Discussion

The goal of this study was to ascertain basic characteristics and limiting operation conditions of the IJE system. Experiments were conducted at different deposition conditions to determine the effects of process variables on particle incorporation. While the process variables were examined independently, they are not necessarily independent. The process conditions studied were flowrate, current density, particle size, and particle loading.

Current Density

At a constant flowrate of 2.5 L/min (0.66 gal/min) and particle loading of 120 g/L (1 lb/gal), current density was varied from 25 to 250 mA/cm² (161 to 1610 mA/in²) to study its effect on incorporation of 50 nm (~2 μ -in.) and 1 μ m (~40 μ -in.) diameter particles. The results of these experiments are shown in Fig. 2. The incorporation of 50 nm diameter particles increased with current density, whereas that of 1 μ m diameter particles generally decreased with current density. It has not been determined whether differences in particle size or crystalline phase are responsible for these contrasting trends. Deposits made above 200 mA/cm² (1290 mA/in²) were of poor quality and could not be evaluated for particle incorporation.

Of all of the IJE process variables, current density was found to have the largest effect on incorporation, which has been also observed for studies with a rotating cylinder electrode (RCE).⁷ However with the RCE, the particle incorporation showed an increase in current density with a maximum at about 25 mA/cm² (161 mA/in²), then a decrease for both particle sizes. Further studies are needed with the IJE to determine whether there is a maximum in the incorporation curve at a low current density. For the IJE, the maximum incorporation of 7.0 wt% at 25 mA/cm² (161 mA/in²) for 50 nm (~2 μ -in.) γ -alumina particles is 60% higher than the maximum of 4.4 wt% at 20

mA/cm² (129 mA/in²) found with the RCE.⁷ This is also nearly 5 times the maximum incorporation of 1.45 wt % at 20 mA/cm² (129 mA/in²) found in previously published results.³¹ Furthermore, this is the highest incorporation of γ -alumina particles to date. Incorporation with a parallel plate electrode configuration typically have been reported to be typically less than 0.1 wt%.²¹

High incorporations with 1 μ m α -alumina were also obtained with the IJE system. A maximum incorporation of 5.3 wt% was observed at 200 mA/cm² (1.3 A/in²) as shown in Fig. 2. In comparison, the maximum incorporation of 1 μ m (~40 μ -in.) α -alumina with the RCE system was only 0.7 wt%.³² α -Alumina has been observed to readily incorporate in copper with a parallel plate electrode configuration,²¹ with the largest incorporation reported for 1 μ m (~40 μ -in.) particles of 8.8 wt% ³³



Figure 2 – Effect of current density on incorporation for 50 nm (~2 μ -in.) γ -Al₂O₃ and 1 μ m (~40 μ -in.) α -Al₂O₃ at a flowrate of 2.5 L/min (0.66 gal/min) and particle loading of 120 g/L (1 lb/gal).

Flowrate

Flowrate has a significant effect on particle incorporation, as shown in Fig. 3 with 50 nm (~2 μ -in.) γ -alumina and 1 μ m (~40 μ -in.) α -alumina particles in copper. Flowrate was varied from 0.5 to 7.0 L/min (0.13 to 1.85 gal/min), a range determined by the limitations of the diaphragm pump. The current density was maintained throughout these experiments at 75 mA/cm² (0.48 A/in²) for a particle loading of 120 g/L (1 lb/gal). For both sizes of particles, a maximum incorporation was found in the 2.5 – 3.0 L/min (0.7-0.8 gal/min) region. In these experiments, flowrate had a more pronounced effect on incorporation for the 50 nm (~2 μ -in.) particles than for the 1 μ m (~40 μ -in.) particles.

These results are quite different from those seen by Takeuchi et al. for incorporation of 0.7

 μ m (~30 μ -in.) SiC particles in nickel with an IJE system.²⁹ For the Ni-SiC system, it was observed that incorporation steadily decreased with increasing flowrate. Since both the 50 nm and 1 μ m (~2 and 40 μ -in.) alumina particles exhibited similar incorporation behavior with respect to flowrate, it is unlikely that differences in SiC and Al₂O₃ particle size caused these differences.

The effect of rotation rate on incorporation in the RCE system was not as significant as the flowrate in the IJE system.³² With the 50 nm (~2 μ -in.) γ -alumina particles and a constant current density of 10 mA/cm² (65 mA/in²) a change of only ~1 wt% incorporation was observed with a decreasing rate of rotation from 1500 to 500 rpm for the RCE. In comparison, there is a nearly 2.5 wt% change in incorporation in the IJE system when the flowrate is varied. Also, above 10 mA/cm² (65 mA/in²) for the RCE, current density becomes the most important variable influencing particle incorporation. Further testing is necessary to determine whether similar behavior occurs with the IJE system.



Figure 3 – Effect of flowrate on incorporation of alumina in copper for 50 nm (~2 μ -in.) γ -Al₂O₃ and 1 μ m (~40 μ -in.) α -Al₂O₃ at a current density of 75 mA/cm² (0.48 A/in²) and particle loading of 120 g/L (1 lb/gal).

Particle Loading

Regardless of the deposition system, particle loading in the suspension has been shown to have a significant impact on incorporation.²¹ To determine the effects of particle loading on incorporation,

depositions were performed at 75 mA/cm² (0.48 A/in²) and 2.5 L/min (0.66 gal/min) with loadings of 20, 40, 80, and 120 g/L (0.16, 0.39, 0.49, and 1 lb/gal) as shown in Fig. 4. Maintaining the particles in suspension above 120 g/L (1 lb /gal) was difficult for the IJE system; 158 g/L (1.31 lb/gal) was found to be the maximum possible loading in studies with the RCE.³² Significant incorporation was seen with particle loadings as low as 20 g/L (0.166 lb/gal), where incorporation was found to be 0.8 wt% (which approaches the limits for the electrogravimetric method used to determine particle incorporation), and increased nearly linearly with increased loading in suspension. Similar incorporation values were obtained in the RCE system with a 39 g/L (0.32 lb/gal) particle loading.³² By using the current density of maximum incorporation, it may be possible to achieve measurable incorporation with particle loadings below 20 g/L (0.166 lb/gal). To date, no other work on the effects of particle loading on incorporation in the IJE system has been published.



Figure 4 - Influence of particle loading on incorporation of 50 nm ($\sim 2 \mu$ -in.) γ -Al₂O₃ in copper for a flow rate of 2.5 L/min (0.66 gal/min) and a current density of 75 mA/cm² (0.48 A/in²).

Deposit Analysis

SEM was utilized to better understand the distribution of particles within the codeposited films. Fig. 5 is a backscatter image taken of the substrate side of a deposit made at 150 mA/cm² (0.97 A/in²), 2.0 L/min (0.53 gal/min), and particle loading of 120 g/L (1 lb/gal). The incorporation of 50 nm (~2 μ -in.) γ -alumina particles in this sample was 1.2 wt%. The alumina particles appear as

dark spots in a lighter copper matrix, as verified by energy dispersive spectrometry (EDS). Fig. 5 shows a homogenous distribution of particles within the copper matrix. It should be noted that particles appear to be incorporated both individually and as agglomerates. Using additives may be useful for improving the dispersion of larger agglomerates.



 Figure 5 - Backscatter electron image of a composite film made at 150 mA/cm² (0.97 A/in²) and 2.0 L/min (0.53 gal/min) with 50 nm (~2 μ-in.) γ-Al₂O₃particles (shown as dark spots).

Summary & Conclusions

The main goal of this work was to develop an unsubmerged IJE system and to determine the general effects of process parameters at the limits of the system operation on the incorporation of alumina particles into a copper matrix. The process variables studied included current density, flow rate, particle loading, and particle size. All of these factors were found to significantly influence particle incorporation. Current density, which was varied from 25 mA/cm² to 200 mA/cm² (0.16-1.3 A/in²), was found to have an opposite effect on the incorporation of 50 nm (~2 µ-in.) γ -alumina and 1 µm (~40 µ-in.) α -alumina particles. While incorporation of γ -alumina decreased with increasing current density, it increased for α -alumina under the same conditions. At a flowrate of 2.5 L/min (0.7 gal/min), a maximum incorporation of 6.9 wt% was achieved for α -alumina at a current density of 25 mA/cm² (0.16 A/in²). At the same flowrate, a maximum incorporation of 5.3 wt% was obtained for γ -alumina at 200 mA/cm² (1.3 A/in²). In contrast, similar trends were

observed for both sizes of alumina particles as a function of flow rate, but with higher levels of incorporation for the 50 nm particles. For these experiments, a maximum incorporation was found at approximately 2.5-3 L/min (0.7-0.8 gal/min). Lastly, increasing particle incorporation was found to increase linearly with particle loading in the bath. Surface morphology was studied using SEM. From these images, it was observed that the particles were incorporated both individually and as agglomerates.

Future work will study the effects of the process variables of the IJE system on particle incorporation in detail. Also, the effect of bath composition and additives will be studied.

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