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# Electrolyte Design for Suspended Particulates in Electrolyte Jet Processing

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The addition of particles (<1 $\mu$ m) to electrolyte feedstocks results in marked changes to the morphology of deposits when Electrolyte Jet Processing (EJP) compared to electrolyte only feedstocks. Through the use of a 'carrier' electrolyte in additive mode these particulates may become embedded within a deposited matrix. These also serve as nucleation points for crystallisation. This allows opportunities for creating complex surface coatings and incorporating materials independent of crystallisation phenomena. Control of the microscale morphology of these is demonstrated here through the addition of the brightening agent - thiourea and the buffer - sodium sulfate. Here acidity and hence electric surface potential are modified and the response upon deposition evaluated.

Electrolyte Jet Processing, composite plating, nano-suspensions

## 1. Introduction

Plating processes are commonly used for the deposition of metallic coatings to create robust engineering surfaces. The use of the plating media to act as a carrier for fine particles represents a useful augmentation to this process and is referred to as composite plating [8]. The use of suspended particles within electrolyte jet processing techniques has also been shown to be possible and the fluid dynamics [REF], chemistry [REF] and morphology [REF] of deposits have been investigated. Typical plating investigations have focussed upon the co-deposition of Nickel and ceramic reinforcements to create metal matrix ceramic (MMC) coatings which provide both corrosion and wear resistance. However, this principle can be used for the deposition of several metals through the dissolution of a metal salt and electrolytic plating but the pallet of materials available is largely limited due to the practicalities of handling hazardous salt solutions. Increasingly, surface scientists seek manufacturing technologies which can produce functionalised surfaces through the incorporation of nano-particles. This forms the inspiration for this work.

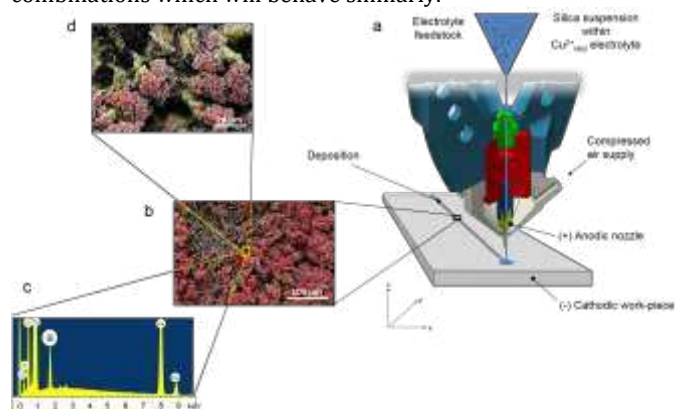
The design of the carrier electrolyte used in jet processing has a significant effect on the morphology of the deposit and also the distribution of the reinforcement. Agglomeration within micro and nano-particulate suspensions is widely reported [7]. The formation of agglomerates has the undesired effect of producing an uneven distribution of reinforcements (see Figure 1).

In this study Silica nano-particles were suspended within copper sulphate electrolytes and the effect of electrolyte concentration and acidity was investigated following attempts to improve deposits through the use of the brightening agent - thiourea and controlling the pH with the addition of sulfuric acid and the buffer sodium sulfate.

A typical EJP arrangement is shown in Figure 1. Here, silica particles are depicted in a suspension to be delivered via a jet formed through expulsion of an electrolyte through an anodic orifice. Using simple copper sulfate solutions with suspended silica particles results in structures shown in Figure 1b. These exhibit non-uniform distributions of Silica (yellow) and a rough - fractal type morphology. Overcoming these limitations is the primary objective of research presented here.

In this work, it is proposed that copper electrolyte concentration, when used alongside the additives thiourea and sodium sulphate, can stabilise the deposition of copper surface films at moderate pH conditions yielding a more even deposition of higher purity, when used in conjunction with optimised processing parameters. In addition the electrochemical jet processing of copper at lower acidity allows for the colloidal stabilisation of nanoparticle silica within the electrolyte and consequently co-deposition is not inhibited and the

hydrophilicity of the silica nanoparticles is retained resulting in a more consistent and well distributed composite. This material system is proposed as a useful demonstrator for other material combinations which will behave similarly.



**Figure 1** Suspending particles within an EJM electrolyte allows for MMC deposition a) General arrangement of EJP apparatus used in this study b). The characteristic highly localised Silica agglomerations resulting from a poor dispersal within an electrolyte. c). EDS spectra highlighting the formation of a Silica encased in a copper matrix d) regions highlighted yellow show Si incorporation

## 2. Materials and Methodology

### 2.1. Experimental Apparatus

In this study an electrolyte jet processing apparatus was used which allows for the delivery of electrolyte over planar surfaces using a 3-axis arrangement. This apparatus is detailed elsewhere [9] and shares common features with machines used by Kunieda et al. [6] and Hackert et al. [5]. In the configuration used here for deposition, the nozzle acts as the anode and the work-piece as the cathode in the electrolytic cell. A constant electrolyte jet, exiting a 500  $\mu$ m I.D. nozzle at 16 m/s was used throughout this study for interactions of XX ms. The nozzle tip was maintained 500  $\mu$ m from the incident surface. Focusing of the jet is assisted by a 3 bar co-axial air shroud around the jet. This ensures the jet spread on impingement is minimised. Current density [2] measured at the nozzle tip, was varied throughout the trials from 5 A/cm<sup>2</sup> to 50 A/cm<sup>2</sup>. Here constant masses of SiO<sub>2</sub> were added to the feedstock electrolytes to assist in the design of the carrier electrolyte and also to ensure that variations in loading did not serve to modify the fluid mechanics or conductivity of the electrolyte. Silica containing electrolytes were magnetically stirred throughout processing to maximise colloidal dispersion.

### 2.2. Preparation of Materials

Commercially pure copper substrates were used in this study and were acquired from Smiths Metal Centres Ltd. Surfaces were ground with 1000 grit paper, followed by washing with deionised

water.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Fisher),  $\text{Na}_2\text{SO}_4$  (Fisher),  $\text{H}_2\text{SO}_4$  (Fisher), thiourea (Sigma Aldrich) and silica nanoparticles (200 - 300 nm, Sigma Aldrich) were used in this investigation. Composition and pH ranges for the electrolytes used here are given in Table 1. All chemicals were analytical reagent grade or higher. After processing, samples were rinsed with deionised water and dried prior to further characterisation.

**Table 1** The composition of electrolytes used in this study for spot deposition and analysis

Trial set	Chemical	Composition ranges
<b>Meso behaviour</b> (thiourea addition)	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ $\text{Na}_2\text{SO}_4$ Thiourea Silica powder	0.5 M 0.25 M 0.14 - 6.57 mM 0.3 g/L
<b>Nodule sizing</b> (pH variation)	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ $\text{Na}_2\text{SO}_4$ $\text{H}_2\text{SO}_4$	0.1 - 0.662 M 0 - 1 M pH 2 - 4.5
<b>Surface charge</b> (Zeta Potential)	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ $\text{H}_2\text{SO}_4$ Silica powder	0 - 0.05 M pH 2 - 4.5 0.1 g/L
<b>Hybrid Electrolyte</b> (sodium sulfate - thiourea combined) -	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ $\text{Na}_2\text{SO}_4$ $\text{H}_2\text{SO}_4$ Thiourea Silica powder	0.02 - 0.5 M 0 - 1 M pH 2 - 4.5 0 - 15 mM 0.3 g/L

In all experiments apart from Zeta potential measurements, silica additions remained constant at 0.3 g/L. Since this process is sensitive to elevated suspension concentrations and pH level these were attenuated in order to evaluate the behaviour of more dilute solutions than those used for deposition.

### 2.3. Surface charge analysis

Electric surface potential or zeta potential is a useful method for evaluating the propensity of colloids to agglomerate in a given fluid [REF]. Ideally a high magnitude zeta potential ( $\zeta > +25\text{mV}$  or  $\zeta < -25\text{mV}$ ) would create the optimum dispersion of colloids within an electrolyte. The moderate negative zeta potentials of hydrophilic silica particles reported in acidic conditions [1] implies that silica dispersion will be poor in co-deposition with copper, which is acidic. Additionally cupric ions are reported to further reduce zeta potential through shielding the dielectric layer between colloids and the carrier. Copper is conventionally plated in acidic sulfamate baths [ref, ref], which tend to have an acidity greater than pH 4. This avoids excessive surface oxidation of the deposited copper and superior material properties [REF]. Zeta potentials were appraised across a range of  $\text{Cu}^{2+}$  concentrations using a Malvern Zetasizer Nano ZS, which utilises the laser Doppler electrophoresis technique. The movement of the silica particles within an electric field is assessed through measurement of small frequency shifts,  $\Delta f$ , in the scattered laser light (of a wavelength  $\lambda$ ) according to Equation 1. From the frequency shift ( $\theta$ ), the velocity,  $v$ , and therefore the magnitude of surface charge of the silica nanoparticles within a given solution can be appraised.

$$\Delta f = 2v \sin \frac{\theta}{2} / \lambda \quad (1)$$

### 2.4 Analysis of Deposits

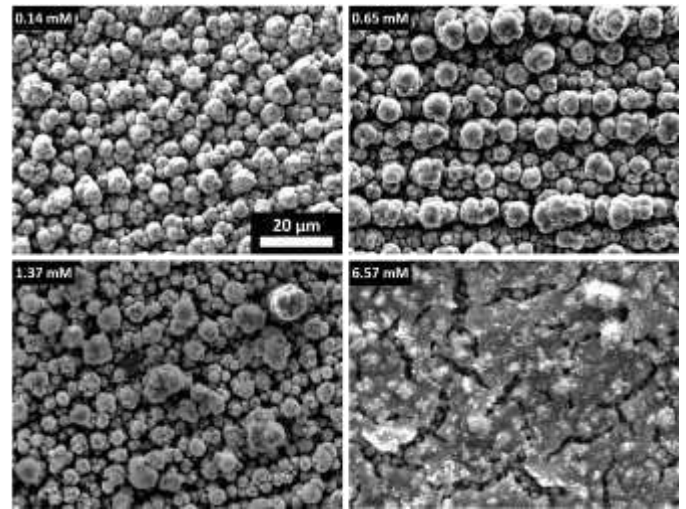
Scanning electron microscopy (SEM) was performed using Philips XL30 and Hitachi S2600 N instruments (both thermionic sources). Energy dispersive X-ray spectroscopy (EDS) was undertaken using an Oxford Instruments X-Max 80 SDD EDS system. Interferometry was carried out using an Alicona Infinite Focus G5 focus variation microscope to generate 3D areal surface data of selected deposits. The diameters of nodular features in electrodeposited copper were sized manually using the scaling

function in ImageJ software and histograms were generated from the data acquired from 300 nodules for each electrolyte.

## 3. Results and Discussion

### 3.2. Improving Meso Behaviour

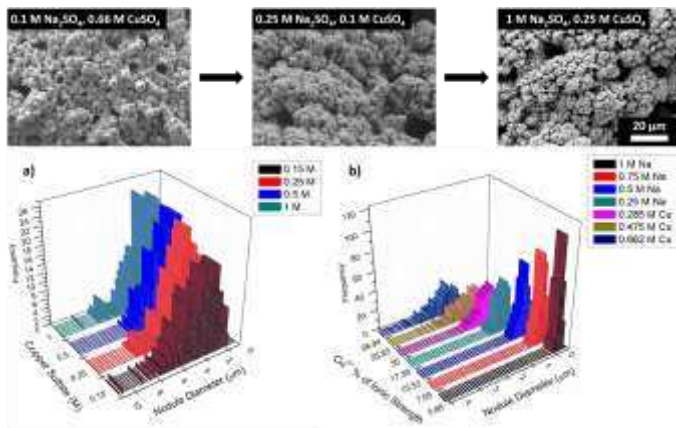
In order to demonstrate control of surface morphology thiourea was added to electrolyte feedstocks. Critically, deposits are observed to go from discontinuous nodule type structures toward a more continuous deposit with increasing concentrations of thiourea. Each nodule is associated with the initiation event and growth of an individual crystal. While a continuous coating is the primary objective of this study a mechanism for controlling the surface morphology of deposits is possible. Alignment of nodules here is consistent with the underlying ground surface texture of the substrate. This also serves to demonstrate the capability of this technique to generate structured surfaces upon a template surface.



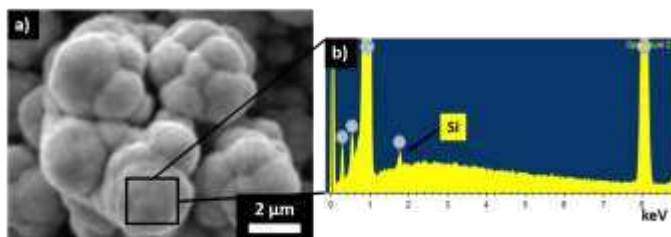
**Figure 2** Through the addition of thiourea to the electrolyte the morphology of EJM deposits can be modified. Note the transition of discontinuous nodule growth evolution through to the creation of a near continuous surface with increasing concentration. A poor distribution of Silica is observed (light patches in 6.57mM concentration).

In deposits created through the use of thiourea concentrations of 6.57mM a distinct surface morphology is evident in the central region of deposits where current density is highest. At high concentrations it is possible to observe agglomerates of silica (lighter coloured regions) at the near surface of the deposit. This represents an undesirable coating as local ceramic concentrations will serve to diminish the integrity of the coating while limiting the ability of the surface to be later functionalised [REF]. The nodule size resulting from thiourea addition to the feedstocks was shown not to vary significantly with concentrations investigated evidenced in Figure 3a. Here nodules were measured from SE micrographs (x3200) and measured over constant areas (95 x 70  $\mu\text{m}$ ) and further evaluated using ImageJ image recognition software.

Figure 4 shows a typical high magnification micrograph (x25K) of a single nodule structure.



**Figure 3** Nodule size frequency histograms of the deposit jet core, deposited at 50 A/cm<sup>2</sup>, a) limited change in size and distribution of nodule sizes across a broad range of CuSO<sub>4</sub> concentrations (and therefore conductivities), where the copper contribution to the total ionic strength of the electrolyte is reduced nodules are enlarged and distribution is narrowed b).



**Figure 4** Nodule composition is shown to be constituted of both Cu (matrix) and SiO<sub>2</sub> (suspended) and as such nodules are limited.

A fractal type structure can be observed in all deposits which is typical of crystallisation phenomena of copper. Mean nodule size across concentrations is ~2.2 μm. Therefore, there is no apparent sensitivity of the process to changing concentrations.

The mechanism by which transition migrates from primarily nodular morphology to a near continuous surface relates to the adsorption of sulfur-containing groups at crystallisation sites. This results in higher localised resistance and preferential crystal growth in other sites and hence a more even distribution [ref or substantiation].

With addition of sodium sulphate, Figure 3b, the ionic strength of the electrolyte results from a combined contribution of the copper sulfate but also the sodium sulfate in these electrolytes. In Figure 3 the effect of sodium sulfate addition on nodule size is shown. Increasing the contribution to ionic strength from the copper cation increases the mean nodule diameter and also creates a broader distribution.

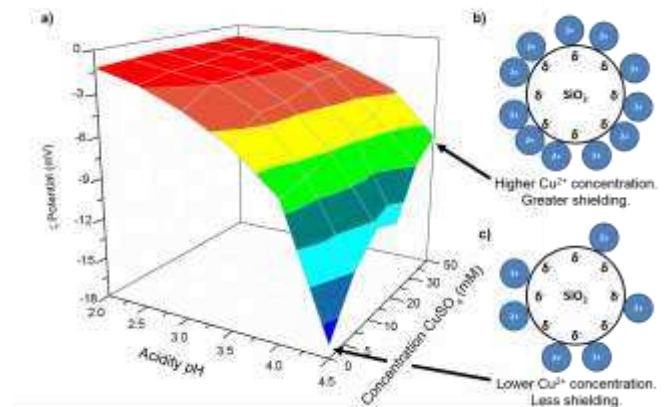
At higher contributions to ionic strength from copper as opposed to sodium the smaller nodule size is observed due a higher purity in the deposit which promotes nodule formation.

Greater contributions to the ionic strength from the sodium content in the electrolyte allow some modulation of nodule size but the purity of the deposit will be adversely effected and hence crystallisation is more stochastic and free growth is arrested and smaller nodules are observed. These observations create a means by which the nodule size within a deposit can be modulated. While practitioners may seek to deposit continuous surfaces emerging applications may make use of fractal type surface structures.

### 3.3. Surface charge considerations

In order to create superior distributions for the reinforcement media within the composite the zeta potential across a range of concentrations and pH levels was evaluated. Consistent with the

theory [Ref] for suspended silica colloids in solution a higher pH is shown to dramatically reduce zeta potential magnitude and hence the repulsive force between particles. This creates a problem and agglomerations will form. In order to evaluate this effect in the electrolytes in question zeta potential was measured over a range of pH values obtained through the addition of sulfuric acid and varying concentrations of copper sulfate. Figure 5. Shows a clear trend dominated by the pH as opposed to the copper sulfate concentration although some shielding effect is evident.



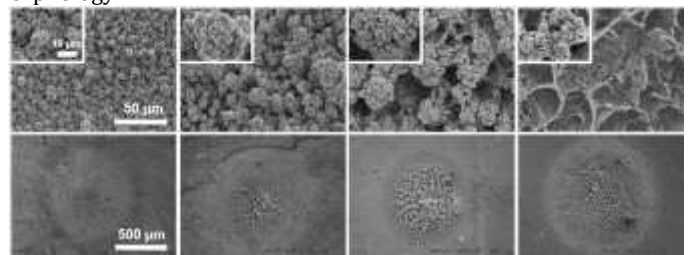
**Figure 5** a) Combinatory relationship of acidity and concentration upon the zeta potential of the electrolyte serving to demonstrate the ability of the carrier electrolyte to provide uniform suspensions of particulates within an electrolyte b) and c) the mechanism of surface charge neutralisation through electrostatic shielding in a high and low concentration Cu<sup>2+</sup> electrolyte respectively. Surface charge tends towards positive values in acidic solutions as a result of the protonation of surface silanol groups.

Shielding through higher concentrations of copper sulphate also lowers zeta potential. Concentrations evaluated here are lower than those typically used for bulk plating or jet processing but a precision electrolyte has been sought here at the cost of mass deposition rate. This allows for electrolytes to be designed with a more even distribution of the particles within the electrolyte and should reduce the agglomeration phenomena within deposits.

The use of low concentrations to arrive at a relatively stable silica suspension with impact upon the charge carrying ability of the electrolyte and limit deposition rate but superior deposits will be observed at lower current densities. [REF]

### 3.4 Deposition Observations

In evaluating the integrity of electrolyte jet deposits porosity is a key concern. Electrolytes were prepared with graduated concentrations of copper sulfate and sodium sulphate (see Table 1) was used as a buffer to control pH and as a result, the zeta potential of the feedstock. In Figure 6 the effect increasing concentrations has upon the deposit morphology is clearly seen. Nodule morphology is observed to be reduced with increasing sodium sulfate concentration. In addition deposition efficiency (larger deposits) is increased alongside an evolution in nodule morphology.



**Figure 6** The evolution of nodule and deposit formation with the addition of sodium sulfate - xM, yM zM from left to right. Nodule size is shown to decrease. These were

