Voltammetric anodic dissolution (VAD) applied to the quantitative analysis of coating discontinuities – influence of electrodeposition parameters

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Abstract

A voltammetric anodic dissolution (VAD) technique was used to quantify disruption and fault levels in nickel deposits on a copper substrate. This technique was based on a comparison of the charge passivation densities of the substrate with and without coating. The chosen system was electrolytic nickel coating on copper substrate, applied from a commercial Watts bath without additives under galvanostatic conditions. The results show the VAD technique to be useful in detecting variations in coating porosity and discontinuities caused by different applied deposition currents and charge densities. A minimum of porosity level was also detected in coating thicknesses obtained at a charge density of about 1200 mC cm^{-2}. With higher deposition charge densities, a coating fragmentation process (disruption) generating spheric-like particles was observed.

1. Introduction

Some causes of coating porosity are attributable to the precleaning process, surface rugosity, the shape of the piece being plated, the metallurgical condition of the surface (metallic and nonmetallic inclusions) and hydrogen bubbles generated during plating [1–3]. In addition, an electroplated metal is usually subjected to tensile or compressive stress due to mismatching of the lattice parameters of the electroplated and substrate materials. The measurement of these forces has been a subject of considerable interest in the electroplating industry, because they can cause coating cracking and adversely affect properties [4–6].

Defects in electroplated layers can be classified as follows:

- Pores located in areas never covered by a coating layer – caused by lack of deposition;
- Cracks located in areas where the coating layer undergoes a cracking process – these processes, caused by internal stresses or service loads, lead to exposure of the underlying substrate;
- Discontinuities produced by some chemical or physical attack during service.

One of the main effects observed in metals electrodeposited under high current density conditions is the formation of dendritic structures or powdery deposits. This morphology is associated with the electrocrystallization process and with interactions between substrate and coating [7]. In the case of the nickel/copper system, these interactions present no significant effects due to the similarity of their lattice parameters and crystalline structure (CFC) [8].

The main cause of discontinuities in the nickel/copper system derives, therefore, from coating misfitting or cracks quantified by electrochemical porosity measurement techniques [5, 9]. Correlations between electrodeposition process parameters, such as applied current and charge densities, and coating discontinuities can be estimated [10, 11].

The purpose of this study was to correlate several electrodeposition conditions involving the application of low and high deposition current densities and different deposition charge densities (coating thickness) with the

morphology and discontinuities of electroplated nickel on copper substrate. The electrochemical technique (anodic voltammetry) applied here sheds further light on morphological changes in the coating and aspects of coating discontinuities.

2. Experimental procedures

The electrochemical technique used in this work was anodic voltammetry with measurement of the charge densities involved in substrate and substrate/coating passivation processes [10, 11].

The application of this technique requires a few specific conditions. First, the substrate must not react chemically in the dissolution/passivation solution. Second, the substrate must be passivated when anodically polarized. Third, the coating must remain inert or react only slightly in the potential range of substrate passivation [10, 11].

Nickel coating on a copper substrate system was selected for this study. The nickel and copper bulk electrodes employed here to define the initial conditions were 99.9% purity grade. The small nickel working electrode was cylinder shaped, with an area of 0.226 cm^2, glued inside a Pirex™ glass tube with Araldite™ epoxy resin, with a pre-soldered copper wire for electrical contact. The working copper electrode was built by the same procedure as that used for the nickel electrode, with a cross-sectional area of 0.156 cm^2. The counter-electrode was a 1 mm diameter spiral platinum wire and the reference electrode was Hg/Hg$_2$Cl$_2$/KCl (sat) with a potential of 241.5 mV relative to the standard hydrogen electrode. The equipment used in this work was a PAR potentiostat/galvanostat, model 273 coupled to a computer through the M270 software program.

The nickel electrodeposition process was carried out at three different current densities in galvanostatic mode (1.0, 3.0 and 6.0 A dm^{-2}) and five different deposition times (DT, 10, 20, 30, 40 and 50 s) for each current density. The electrolyte used for nickel deposition was a Watts bath without organic additives, composed of 0.9 M nickel sulfate (NiSO$_4$ · 6H$_2$O), 0.2 M nickel chloride (NiCl$_2$ · 6H$_2$O) and 0.5 M boric acid (H$_3$BO$_3$). The electrolyte used in the anodic polarization process was a 0.5 M sodium sulfide solution (Na$_2$SO$_3$). All the reagents were of analytical grade and the solutions were kept at ambient temperature (25 ± 3 °C). Distilled water was used to prepare the solutions and wash the electrodes. The substrate was polished to grade 1 μm Al$_2$O$_3$. The sweep rate was 10 mV s^{-1}.

The porosity index was obtained by comparing the passivation charge density of the substrate without coating (standard passivation charge density) with that involved in the passivation of the covered substrate, according to the following expression [10, 11]:

$$\theta_i = \frac{Q_{PASS} - (1 - \theta_{i-1})Q_{REV}}{Q_{PASS}^0} \times 100 \qquad (1)$$

where θ_i is the porosity in the ith interaction; θ_{i-1}, the porosity in the previous iteration; Q_{REV} the dissolution/passivation charge for pure coating; Q_{PASS}^0, the standard passivation charge density for uncoated substrate and Q_{PASS}, the dissolution/passivation charge for coated substrate.

3. Results and discussion

To analyze the nickel coating porosity using Equation 1, a previous study of the voltammetric behavior of nickel and copper in the dissolution/passivation solution was required in order to identify the potential ranges for the anodic reactions. As mentioned elsewhere, application of the voltammetric anodic dissolution (VAD) technique requires that the substrate passivates with the coating, remaining inert during the substrate passivation process.

In the case of the copper electrode without nickel coating (Figure 1), the passivation process was found to begin around −0.43 V. The peak of the passivation process occurred close to −0.25 V, with a peak current of 3.4 mA cm^{-2}.

The anodic reaction of the pure nickel electrode (Figure 2) started at approximately −0.50 V, but the charge density in this initial nickel dissolution process was closer to 25 μA cm^{-2}. This reaction was considered insignificant, at least in the potential range in which the copper passivation process occurs, and was therefore disregarded. The nickel dissolution reaction only became significant at potentials more positive than 0.15 V, when the copper passivation process was almost completed.

Typical voltammetries for the dissolution/passivation process of the Ni/Cu system are depicted in Figure 3, which shows the variation of passivation charge density as a function of deposition charge density and a given deposition current density (DCD) of 3 A dm^{-2}.

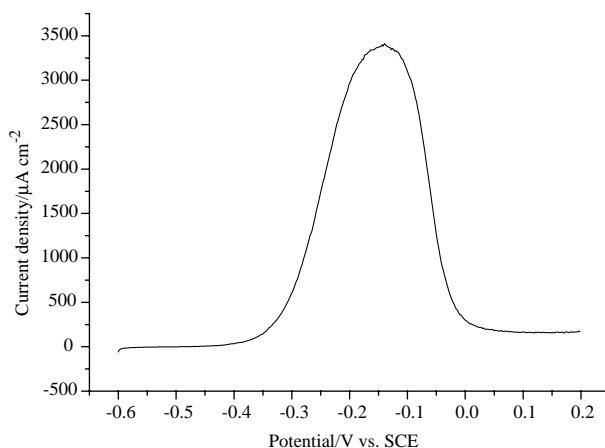The passivation charge density, Q, up to the current density peak, was determined. The degree of disconti-

Fig. 1. Voltammetry: copper electrode, solution: Na$_2$SO$_3$ 0.5 M, sweep rate = 10 mV s^{-1}.
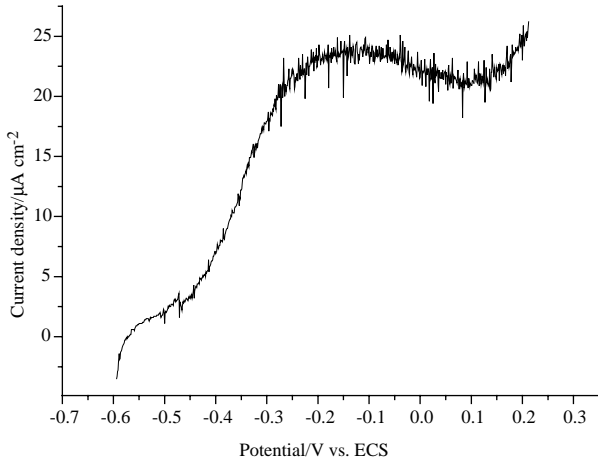
Fig. 2. Voltammetry: nickel electrode, solution: Na_2SO_3 0.5 M, sweep rate $= 10$ mV s^{-1}.

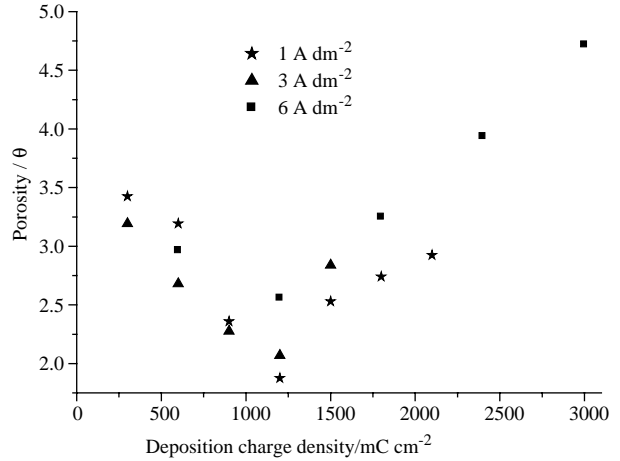*Fig. 5.* Porosity variations as a function of charge deposition density, solution: 0.5 M Na_2SO_3, sweep rate $= 10$ mV s^{-1}.
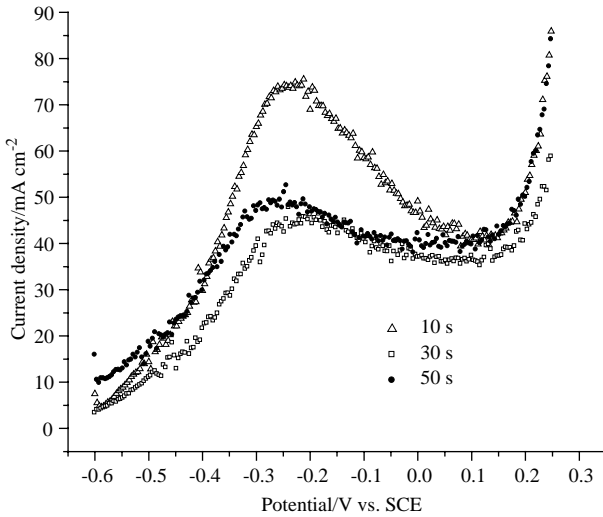

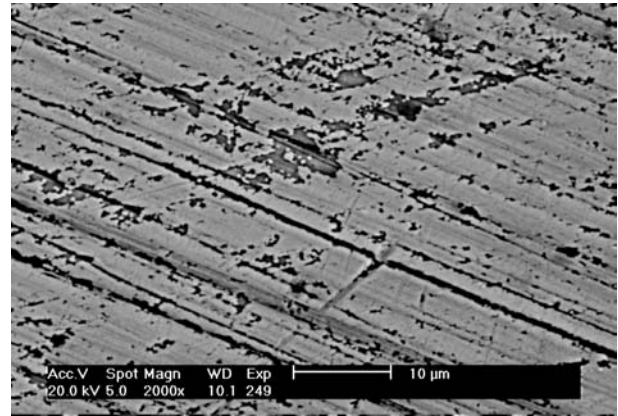*Fig. 3.* Voltammetry: Cu/Ni system, solution: 0.5 M Na_2SO_3, sweep rate $= 10$ mV s^{-1}, DCD $= 3$ A dm^{-2}.

Fig. 6. SEM micrograph of nickel coating on copper substrate. Electrodeposition conditions: Watts bath, 3 A dm^{-2}, DT $= 20$ s.
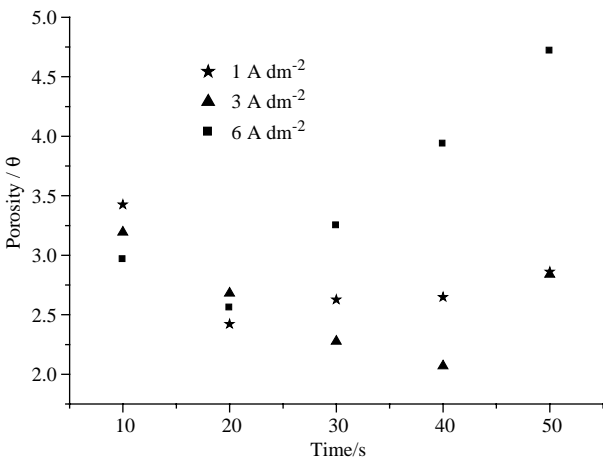

Fig. 4. Porosity variations as a function of DT, solution: 0.5 M Na_2SO_3, sweep rate $= 10$ mV s^{-1}.

nuities, or porosity, of the deposit (θ) was calculated based on Equation 1. Figure 4 represents the variation in porosity/discontinuities according to DT for each applied DCD. An analysis of the resulting curves shows a minimum of discontinuities. This means the coating discontinuities start increasing after a specific thickness is reached.

This behavior is clearly illustrated in Figure 5, where the variation in porosity (discontinuities) was plotted against deposition charge density (Q_{DEP}). The coating disruption began increasing at a Q_{DEP} of about 1200 mC cm^{-2}, independently of the DCD, with the lower coating porosity corresponding to 2% of the total substrate area. A SEM (scanning electron microscopy) analysis of the coating morphology ($Q_{DEP} = 600$ mC cm^{-2}) revealed coating voids (Figure 6). An energy dispersive X-ray (EDX) analysis of this coating revealed that the white zone was nickel while the gray was copper from the substrate (Figure 7). Otherwise, for deposition charge densities greater than 1200 mC cm^{-2}, the morphological analysis showed discontinuity caused by
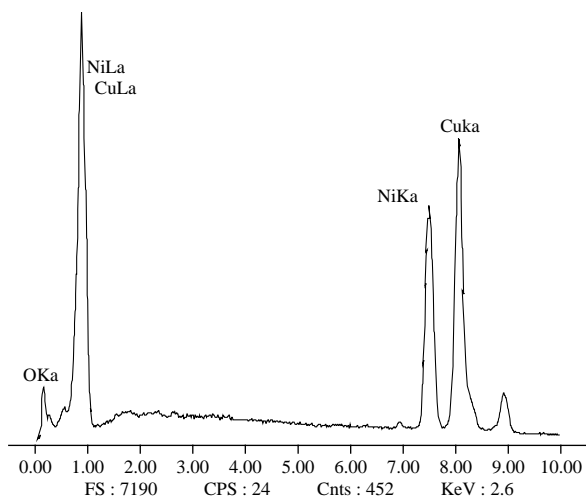
Fig. 7. EDX analysis of nickel coating on copper substrate. Electro-deposition conditions: Watts bath, 3 A dm^{-2}, DT = 20 s.

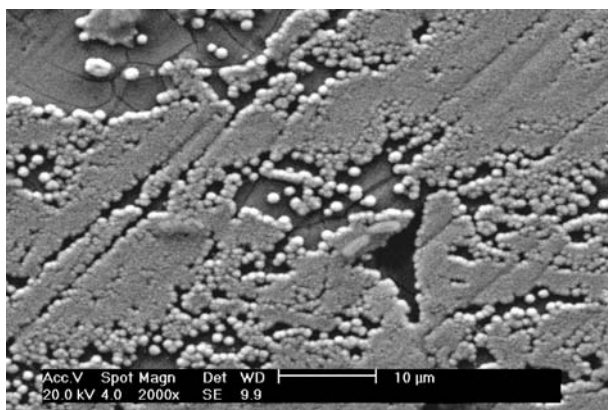*Fig. 8.* SEM micrograph of nickel coating on copper substrate. Electrodeposition conditions: Watts bath, 3 A dm^{-2}, DT = 60 s.

coating disruptions (Figure 8) generating spherical-shaped structures.

4. Conclusions

The results demonstrated that the VAD technique is sensitive to analyses of porosity or discontinuities in coatings produced under various deposition conditions, such as current or charge densities. The cracking process was found to be dependent on the applied current and charge densities, with a minimum of discontinuities occurring closer to 1200 mC cm^{-2}. The MEV and EDX analyses were congruent with the VAD results, with micrographs showing coating faults (or faulty deposition) at charge deposition densities of less than 1200 mC cm^{-2}. At charge deposition densities exceeding 1200 mC cm^{-2} and hence, thicker coatings, the micrographs showed coating disruptions resulting in spherical particles and exposed substrate. The lower porosity level detected by the VAD technique applied to the coating process under study was 2%.

Acknowledgements

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