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Influence of pulse plating parameters on the electrocodeposition of matrix metal nanocomposites

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Abstract

Electrocodeposition of alumina particles with copper and nickel from acidic electrolytes has been investigated using different deposition techniques. Compared to direct current (DC) deposition, both pulse plating (PP) and pulse-reverse plating (PRP) facilitated higher amounts of particle incorporation. With conventional DC plating the maximum alumina incorporation is ~ 1.5 wt% in a nickel and ~ 3.5 wt% in a copper matrix. However, the implementation of rectangular current pulses can give considerably higher particle contents in the metal layer. A maximum incorporation of 5.6 wt% Al₂O₃ in a copper matrix was obtained by PP at a peak current of 10 A dm⁻², a duty cycle of 10% and a pulse frequency of 8 Hz. In general, low duty cycles and high pulse frequencies lead to an enhanced particle codeposition. The microstructure and the hardness of both pure metal films and nanocomposite coatings showed only a weak dependence on the PP and PRP conditions. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Electrocodeposition; Copper; Nickel; Alumina; Nanocomposite; Pulse-plating

1. Introduction

The incorporation of inert particles during metal electrodeposition has stimulated scientific and technological interests for decades [1–3]. Recently, electrocodeposition was industrially used to produce abrasion and corrosion resistant coatings, e.g. for automotive applications [4]. The effect of the operating conditions influencing the quantity of incorporated particles was studied for a variety of interesting metal–particle combinations [5]. Several theoretical models have been proposed to describe the electrocodeposition phenomena [1,3,5–8]. However, up to date the mechanism of particle incorporation is not fully understood. This lack of fundamental understanding of the electrocodeposition process has resulted in a trial and error approach being the only method of developing parameters for industrially applicable codeposition of composite films with fairly reproducible particle content.

The properties of metal matrix composites (MMCs) mainly depend on their composition and structure [9]. Uniform distribution and high amounts of incorporated particles within

0013-4686/\$ - see front matter © 2007 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2007.06.009 the metal matrix were found to be crucial to improve the coating properties [10,11]. In many cases the enhanced performance of the coatings is mainly caused by a change in the growth mode or grain size of the metal matrix [11,12] and not so much by the presence of the particles themselves. The particle incorporation is affected by several interrelated process variables, e.g. current density, pH and bath composition, hydrodynamics and particle size, type and shape [2,13–17]. Furthermore, the time dependence of the applied current is one of the most important parameters in the electrocodeposition process [17].

The structure of electroplated metal and alloy coatings is specified by the electrocrystallization process, particularly by the interplay between nucleation and crystal growth [18]. An attractive way of controlling these two processes is the application of a periodically changing current [19]. Thus the microstructure and the properties of the films can be easily controlled by varying, e.g. cathodic pulse length (t_{on}), pulse pause (t_{off}), cathodic peak current density (i_p), anodic pulse length (t_{rev}), anodic peak current density (i_{an}) and average current density (i_{ave}) [19]. Compared to DC plating, PP can yield nanocrystalline coatings with improved surface appearance and properties, such as smoothness, refined grains and enhanced corrosion resistance [12,20–24].

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	Copper sulfate	Nickel sulfamate	
Metal	$0.8 \text{ M CuSO}_4 \times 5 \text{ H}_2\text{O}$	1.08 M Ni(NH ₂ SO ₃) ₂ ; 0.04 M NiCl ₂ × 6H ₂ O	
Other	0.55 M H ₂ SO ₄ ; 3.26 mM HCl	0.65 M H ₃ BO ₃	
pH	1.7	4.3	
Temperature (°C)	45	40	
Particles in suspension $(g L^{-1})$	0, 1, 5, 10	0, 1, 5, 10	
Total electrical charge (C)	140	140	

 Table 1

 Electrolyte composition and deposition parameters

Besides the electrocrystallization the particle inclusion during MMC plating is affected by pulse plating. It has been observed that PP [15,17,25–27] as well as PRP [28,29] could be used to enhance the particle incorporation. In the case of PRP of Cu–Al₂O₃ composites, the maximum particle incorporation was found when the deposit thickness per cycle approaches the particle diameter [28]. Furthermore, it has been shown in ref. [30] that PRP with pulses in the order of seconds can be used for a size-selective incorporation of alumina nanoparticles into copper matrices. However, the distribution of incorporated particles can be also improved by PP. In the case of Ni–Al₂O₃ composites, pulse plating leads to an incorporation of smaller and less agglomerated nanoparticles [31,32].

There are some reports on the effects of PP and PRP on the electrocodeposition of alumina with copper and nickel from acidic electrolytes [25,27,28,30-33]. Promising improvements in terms of the amount and the distribution of incorporated alumina particles have been reported with a pulse length in the order of milliseconds [27,31,32]. However, no extensive investigations on the effect of the several interrelated PP and PRP parameters, such as t_{on} , i_p , t_{off} , t_{rev} and i_{an} , can be found in the literature. The present paper aims at shedding some light on this issue. The codeposition behavior of γ -Al₂O₃ with copper and nickel was studied using three different electrodeposition techniques. The results of the DC plating experiments were published in detail in previous papers [11,13]. Here we discuss the effect of pulse plating (PP) and pulse reverse plating (PRP) conditions, e.g. pulse frequency, duty cycle and value of the peak current density, and particle loading on the composition and properties of the MMCs. The duration of the employed rectangular current pulses was in the order of milliseconds. The particle content, structure and hardness of the films have been characterized and their dependence on the deposition parameters will be discussed.

2. Experimental

Copper/alumina and nickel/alumina nanocomposites were deposited from an acidic copper sulfate bath and acidic nickel sulfamate bath, respectively. The basic composition of the electrolytes and the deposition parameters are given in Table 1. The Al_2O_3 particles (Aeroxide Alu C, Degussa) with an average size of 13 nm and a specific BET-surface of ~100 m² g⁻¹ were used as received without any further treatment.

Deposition experiments were performed in a three-electrode system with a cell volume of 300 mL. The bath temperature was maintained at $45 \,^{\circ}\text{C}$ using a Haake thermostate (model G

D1, accuracy ± 1 °C). During the electrocodeposition the electrolyte was magnetically stirred at a speed of about 300 rpm in order to keep the nanoparticles in suspension. The anode was a bent plate of pure nickel or copper cylindrically surrounding the working electrode. Copper plates of 2.3 cm² area were used as working electrodes. Prior to the electrocodeposition the substrates were ground using 4000 grade silicon carbide paper, electrochemically degreased and activated with uniclean 675 solution (Atotech Germany GmbH). A potentiostat/galvanostat model 273 (EG&G Princeton Applied Research) was used for the deposition of coatings by dc currents. PP and PRP experiments were carried out using a CAPP pulse-plating system (Axel Akerman S.A., Denmark). After electrodeposition the samples were sonicated in distilled water for 10 min in order to remove loosely adhering particles.

In the pulse deposition experiments the pulse frequency [i.e. $f=1/(t_{on} + t_{off})$] and the duty cycle [i.e. $\theta = t_{on}/(t_{on} + t_{off})$] of the imposed rectangular pulses were varied. The pulse on-time (t_{on}) was varied between 25 and 200 ms and the pulse pause (t_{off}) was kept constant at 100 and 200 ms, respectively (Table 2). For the PP experiments the cathodic peak current density (i_p) was maintained at 5 and 10 A dm⁻², respectively. The overall electrocodeposition times were chosen so that the total charge was always 140 C. This corresponds to a layer thickness of about 21 μ m for the pure metals. In the case of PP depositions the particle content in the electrolyte was varied from 1 to 10 g L⁻¹ Al₂O₃, whereas in the PRP experiments the particle content was maintained constant at 10 g L⁻¹. The cathodic peak current density (i_p) was 5 A dm⁻² whereas the anodic peak current density (i_{an}) varied between 1 and 5 A dm⁻² (Table 3).

Polarization curves in electrolytes with and without particles were recorded using a rotating disk electrode (RDE) at rotation rates of 500 and 1000 rpm and a scan rate of 10 mV s^{-1} .

Table 2
Applied pulse plating current programs

toff (ms)	ton (ms)	Pulse frequency (Hz)	Duty cycle (%)	
25	100	8.0	20.0	
50	100	6.7	33.3	
100	100	5.0	50.0	
25	200	4.4	11.1	
50	200	4.0	20.0	
50	100	3.3	66.7	
200	200	2.5	50.0	
400	200	1.7	66.7	

The cathodic peak current density was 5 and 10 A dm^{-2} , respectively.

t _{on} (ms)	$i_{\rm c} ({\rm A} {\rm dm}^{-2})$	$t_{\rm rev}~({\rm ms})$	$i_{\rm an}$ (A dm ⁻²)	Cu-Al ₂ O ₃ , wt% Al ₂ O ₃	Ni-Al ₂ O ₃ , wt% Al ₂ O ₃
50	5	20	1	3.7	3.1
100	5	20	1	3.5	3.0
200	5	20	1	3.7	3.2
400	5	20	1	4.1	4.8
50	5	20	5	2.7	1.2
100	5	20	5	2.8	1.4
200	5	20	5	3.5	2.4
400	5	20	5	4.0	4.2

Table 3 Pulse-reverse plating conditions and resulting particle incorporation

All samples were plated at a concentration of $10 \text{ g L}^{-1} \text{ Al}_2\text{O}_3$ in the electrolyte.

The working electrode material was a Pt disk (0.2 cm^2) , and the cylindrical counter electrode was of pure copper or nickel. A saturated calomel electrode was used as the reference electrode. All polarization scans were performed by ramping the potential from 0 V down to -1 V (yielding a composite coating of approximately 250 nm thickness) and then anodically to +1 V and back to the starting potential of 0 V.

The surface morphology and microstructure of the coatings were investigated using a Zeiss DSM 982 (Oberkochen, Germany) scanning electron microscope. The samples were embedded in epoxy resin, cut with a diamond saw, mechanically grinded with 800–4000 grade silicon carbide paper and polished with diamond solution down to 1 μ m. Finally, the copper cross-sections were etched with 0.5 M nitric acid and the nickel ones with a mixture of 50 mL concentrated acetic acid and 50 mL concentrated nitric acid. The particle content in the films was determined by energy dispersive X-ray analysis (EDX). The EDX analyses were performed on the surface as well as in the cross-section. The reported values of incorporated Al₂O₃ particles in the copper or nickel matrix are average values of at least three measurements for each sample.

The Vickers microhardness of the films was determined using a FischerScope HM2000 S as described in DIN EN ISO 14577. The reported data are averaged values of 10 measurements. The thickness of all coatings was more than ten times the maximum indention depth of 1 μ m ensuring that effects from the copper substrates are negligible.

3. Results and discussion

3.1. Effect of pulse plating (PP) conditions on the particle incorporation

Electrolytic PP codeposition of alumina particles with copper and nickel was carried out using the current programs shown in Table 2, where the cathodic peak current density was maintained between 5 and 10 A dm^{-2} , respectively.

The variation of the amount of embedded alumina nanoparticles in the metal matrix with the pulse duty cycle is given in Figs. 1 and 2 for various particle contents of the electrolyte. In general, the particle content of the coatings increases with decreasing duty cycle. We found that shorter on times are beneficial for the particle inclusion at the same duty cycle. Depending on the plating conditions, the particle incorporation in copper films ranged from ~1.9 to ~5.4 wt% alumina (Fig. 1a and b) whereas the particle incorporation in the nickel coatings was limited to amounts between ~0.9 and ~2.2 wt% alumina. The maximum particle incorporation of about 5.4 wt% γ -Al₂O₃ was observed in a copper nanocomposite deposited at a duty cycle of 11% and a cathodic peak current density of 10 A dm⁻² (Fig. 1b). Compared to direct current (DC) plating of Cu–Al₂O₃ composites with a maximum particle content of about 3.5 wt% [13], an obvious enhancement of particle concentration occurred due to the application of rectangular current pulses. However, for nickel the improvement of the codeposition is less pronounced when going from DC plating [11] to PP (Fig. 2).



Fig. 1. Effect of the duty cycle on the alumina content of copper-alumina composites electrodeposited at various Al₂O₃ contents in the electrolyte and $t_{on} = 200 \text{ ms.}$ (**II**) 1 g L⁻¹; (**II**) 5 g L⁻¹; (**II**) 10 g L⁻¹. (a) $i_P = 5 \text{ A dm}^{-2}$ and (b) $i_P = 10 \text{ A dm}^{-2}$.



Fig. 2. Effect of the duty cycle on the incorporation of alumina particles in nickel films deposited at various Al₂O₃ contents in the electrolyte and $t_{on} = 200 \text{ ms}$. (\blacksquare) 1 g L⁻¹; (\bullet) 5 g L⁻¹; (\blacktriangle) 10 g L⁻¹. (a) $i_P = 5 \text{ A dm}^{-2}$ and (b) $i_P = 10 \text{ A dm}^{-2}$.

One of the most influential parameters during electrocodeposition is the particle content of the electrolyte [2]. Regardless to the other working conditions, an increase of the alumina concentration in the plating bath leads to an enhanced alumina codeposition (Figs. 1-3). For example, the amount of particle codeposition with nickel was enhanced by about 50% due to an increase of the particle loading of the electrolyte from 1 to 10 g L^{-1} (Figs. 2 and 3). Furthermore, the particle incorporation showed a tendency to increase with the pulse frequency (Fig. 3). In general, the effects of duty cycle and pulse frequency can be explained by the relationship of t_{on} and t_{off} . Decreasing the duty cycle as well as increasing the pulse frequency corresponds to a longer relaxation time, i.e. the time at which no current passes through the system. Hence, due to the longer pause more alumina particles arrive at the electrode without a "concurrent" metal deposition taking place in parallel, and as a result the particle incorporation increases.

The particle content of the nickel nanocomposites increased when the peak current density was decreased from 10 and 5 A dm^{-2} (Fig. 2). In the case of the Cu–Al₂O₃ composites this tendency was less pronounced (Fig. 1). The increase of particle content with decreasing peak current can be explained by the model of Celis et al. which describes the particle codeposition as a multi-step process [7]. According to this model, the particles are transferred to the electrode by means of convection and



Fig. 3. Influence of the pulse frequency on the incorporation of alumina particles at a pulse current density of $5 \text{ A } \text{dm}^{-2}$. (**a**) $1 \text{ g } \text{L}^{-1}$; (**b**) $5 \text{ g } \text{L}^{-1}$; (**b**) $10 \text{ g } \text{L}^{-1}$. (a) Cu–Al₂O₃ composites and (b) Ni–Al₂O₃ composites.

diffusion. Finally, the particle incorporation is mainly governed by the reduction of adsorbed metal ions on the particle surface. In PP deposition, the reduction of free metal ions as well as ions adsorbed on the particles takes place during t_{on} . The rate of metal reduction increases with the absolute value of the cathodic peak current density. Compared to ions adsorbed on the particles free metal ions in the solution have a higher mobility. The increasing peak current density leads to a preferential reduction of free ions at the electrode [26]. Hence, the particle content of the electrocodeposited composite films decreases with increasing peak current density. Independent proof for the adsorption of the metal cations comes from measurements of the zeta potential of alumina particles in sulfate containing solutions [11,13].

The effect of the individual pulse plating parameters (particularly pulse length, t_{on} , pulse pause, t_{off} , and peak current density, i_p) can be summarized by introducing the average plating current density, Eq. (1).

$$i_{\text{ave}} = \frac{t_{\text{on}}t_{\text{p}}}{t_{\text{on}} + t_{\text{off}}} = \theta i_{\text{P}} \tag{1}$$

Taking into account that the average current density increases with the duty cycle, Θ , and peak current density, i_P , one can conclude that the incorporation of alumina nanoparticles is favored by low average current densities. The average current density in PP is comparable to the applied current density in DC deposition. Similar to the currently observed dependence, the maximum



Fig. 4. Anodic polarization curve of as deposited nickel nanocomposites in the acidic nickel sulfamate bath containing various amounts of alumina particles at a rotation rate of 500 rpm. (\longrightarrow) 0 g L⁻¹; (\longrightarrow) 1 g L⁻¹; (\longrightarrow) 5 g L⁻¹.

amount of codeposited particles in the case of DC deposition was often found in the range of low current densities at which the metal ion reduction changes from charge transfer to mass transport control [2,3,33–35]. A maximum incorporation of 5.4 wt% alumina in a copper matrix was achieved at an average current density of about 1 A dm^{-2} and a particle content of 10 g L^{-1} alumina in the electrolyte. In comparison a copper composite film prepared under the same conditions with DC plating at a current density of 1 A dm⁻² contained only ~0.3 wt% alumina.

3.2. Pulse-reverse plating (PRP) of nanocomposites

As a preliminary test polarization curves in the copper and nickel electrolytes were measured using an inert Pt rotating disk electrode (see Section 2). Fig. 4 shows the anodic polarization behavior obtained in the acidic nickel sulfamate bath. An important result was that the anodic polarization is significantly affected by the addition of alumina nanoparticles to the electrolyte. In accordance with the literature [25,34], the presence of alumina nanoparticles in the electrolyte caused a shift of the anodic dissolution peak to more cathodic potentials and a significant increase of the anodic dissolution current density (Fig. 4). The magnitude of both, the shift of the peak as well as the increased anodic current density strongly depends on the alumina concentration in the electrolyte and on the rotation rate of the electrode. Thus, due to an increasing particle loading from 1 to $5 \text{ g L}^{-1} \text{ Al}_2 \text{O}_3$ the maximum stripping current increased from ~ 0.8 to ~ 4.9 A dm⁻² (Fig. 4). This finding can be rationalized with an reduced tendency for passivation of the nickel films and an abrasive effect of the alumina particles in the solution during the anodic nickel dissolution. The following discussion is based on the hypothesis that short phases of anodic dissolution are beneficial for the codeposition process.

The PRP conditions were optimized to obtain deposits with a smooth surface morphology and are given in Table 3. The achieved particle contents are significantly higher than those of the composites plated with DC [11,13] and in the case of nickel also higher than the PP plated films (Figs. 2 and 3). If the duration of the cathodic and the anodic pulse is kept constant the composites plated with a lower anodic peak current density incorporate more alumina particles (Table 3). The amount of dissolved metal increases with the reverse pulse current density and the amount of dispersed particles (Fig. 4). Hence, the particle incorporation seems to be favored by anodic cycles with little metal dissolution. Another interesting observation is that the alumina content of the composites is greatly enhanced at longer cathodic pulse times. Assuming 100% current efficiency for the anodic dissolution, 0.07 and 0.35 nm of nickel are dissolved during one cycle at an anodic current density of 1 and 5 A dm⁻², respectively. In the case of copper the thickness of the dissolved metal layer during stripping cycle is comparable, due to the similar values of atomic mass and density of both metals.

The results shown in Table 3 indicate that the amount of codepostied particles increases with the duration of the cathodic pulse. Furthermore, a lower anodic peak current density and thus a smaller amount of dissolved nickel leads to an increased particle incorporation. The highest incorporation achieved in this study was 4.8 wt% Al₂O₃ in nickel deposited at $i_P = 5 \text{ A dm}^{-2}$, $t_{on} = 400 \text{ ms}$ and $i_{an} = 1 \text{ A dm}^{-2}$, $t_{rev} = 20 \text{ ms}$.

This corresponds to a deposition of about 7 nm (equivalent to the radius of one alumina nanoparticle) followed by the dissolution of 0.07 nm nickel. One can assume that most particles that were captured during the cathodic cycle stay in contact with the electrode during the stripping cycle [27]. This sticking process would be facilitated by induced polarization forces between the particle surface and the surface of the growing composite [27]. Thus, PRP with properly chosen parameters leads to a selective metal dissolution and an effective increase of the particle content of the layer.

It has been reported [27,28] that the maximum particle incorporation during PRP was found when the metal deposit thickness approaches the particle diameter size. In the case discussed above only half of the particle volume is incorporated during the cathodic pulse. Hence, it might be possible to further increase the amount of alumina incorporation by increasing the metal layer thickness per cathodic cycle. However, increasing both i_P as well as t_{on} resulted in deposits with a powdery appearance which did not adhere well to the substrate.

3.3. Surface morphology and microstructural characterization

The surface morphology of pure copper films plated with different deposition techniques is shown in Fig. 5. For DC plating the surface morphology of the copper film is made up of relatively large grains (Fig. 5a). In the case of PP (Fig. 5b) and PRP (Fig. 5c) the surface morphology of the copper coating was only slightly affected by the pulse parameters (t_{on} , t_{off} , i_p , t_{rev} and i_{an}). This finding is at first glance hard to rationalize, because one might assume that due to the application of PP and PRP the crystal growth mode and the surface morphology of the copper matrix change significantly [13,24]. According to the electrocrystallization as discussed in detail by Budevski et al., the grain size and growth mode is defined by the interplay of nucleation and growth [18]. In the case of PP and PRP experi-



16 2 8

Fig. 5. Surface morphology of pure copper films prepared by different deposition techniques. (a) DC, 10 A dm⁻²; (b) PP, $\theta = 67\%$, f = 1.67 Hz, $i_P = 10$ A dm⁻²; (c) PRP, $i_P = 5$ A dm⁻², $t_{on} = 50$ ms and $i_{an} = 1$ A dm⁻², $t_{rev} = 20$ ms.

ments the number of atoms deposited during one cathodic cycle is defined by t_{on} and i_p . Furthermore, sorption processes occurring during pulse pause may influence nucleation and growth processes in the following cathodic pulse cycle [18]. In our PP and PRP experiments (Tables 2 and 3), the cathodic pulse current density is comparable to the average current density in DC plating. Finally, the cathodic overpotential during PP and PRP is close to that obtained during DC plating. Hence, the surface morphology of the copper film is expected to be similar for the different deposition techniques, i.e. DC, PP and PRP (Fig. 5).

The surface morphology of the electrodeposited nickel films, i.e. the size and the shape of the grains were significantly reduced and altered due to both, PP conditions and incorporation of alumina nanoparticles (Fig. 6). In the case of Ni-Al₂O₃ composites (Fig. 6b and d) the agglomerates of alumina particles appear as bright spots in the dark nickel matrix, as validated by energy dispersive X-ray spectroscopy. The nickel growth is affected by several interfacial inhibitors such as H2, Hads, Ni(OH)₂ [20,36,37]. It is assumed that PP conditions as well as particle incorporation perturb the nickel growth and induce an increase of the number of nucleation sites resulting in a refined grain structure [5,31,38,39]. Thereby the perturbation of the nickel growth results from a change in the adsorption-desorption phenomena at the nickel/electrolyte interface which is probably caused by an local pH increase induced by an adsorption of H⁺ on the dispersed particles [17,36].

In the case of nickel electrodeposition from an acidic sulfamate bath, a bimodal grain structure of "truncated pyramidal type" could be observed [11,40] (Figs. 6a and c). A cluster of fine grains surrounds relatively large grains. The PP coatings showed a smooth surface with fine grains (Figs. 6a and c). The pure nickel films plated at a higher pulse current density (Fig. 6a) and longer pulse on-time exhibited a coarser grain structure. Higher values of the peak current density and cathodic pulse length correlate with an increased average current density (Eq. (1)). Hence, the coarsening of the nickel structure with increasing current density is in good agreement with the results for nickel plated from an acidic sulfamate bath under DC conditions [11,41].

Figs. 7–9 show cross-sectional SEM micrographs of pure metal films and metal matrix nanocomposites plated by means of PP and PRP. Regardless of the deposition technique, the pure copper and nickel films exhibited a columnar structure belonging to the field-oriented texture (FT) type [11,13] (Figs. 7a, 8a and 9a). The codeposition of Al₂O₃ particles strongly affects the microstructure of the metal matrix. As a result of the Al₂O₃ addition to the plating electrolyte the microstructure of the copper and the nickel matrix changed to the UD (unoriented dispersion) type (Figs. 7b, 8b and 9b) [11,13,42].

An increase of the average plating current density affects copper and nickel in a different way. A general observation was that with increasing cathodic pulse current density and amount of incorporated alumina nanoparticles a refinement of the copper grains occurred. However, the differences in the microstructure were more pronounced in the case of the PP plated films. The changes of the columnar microstructure were directly related to the refinement of the surface morphology due to an increase in the plating current density [13,43]. In contrast to this, an increase of the average plating current density induced an obvious coarsening of the field-oriented nickel structure (micrographs not shown), which is directly related with the coarsening of the sur-



Fig. 6. Surface morphology of pure Ni and Ni–Al₂O₃ composites plated at a duty cycle of 67% and a pulse frequency of 1.67. $0 \text{ g L}^{-1} \text{ Al}_2\text{O}_3$: (a) 10 A dm^{-2} , (c) 5 A dm^{-2} . 10 g L⁻¹ Al₂O₃: (b) 10 A dm^{-2} , (c) 5 A dm^{-2} .

face morphology (Fig. 6). Of course, SEM does not provide the best microstructural analysis. For an extensive characterization of the grain size distribution and the crystallographic texture TEM and XRD investigations are needed which are currently under way in the authors' lab.

3.4. Microhardness of electrodeposited nanocomposites

The microhardness of the nickel coatings plated under PP and PRP conditions varied between 250 and 520 HV (Fig. 10b), whereas the hardness values of pure nickel films were between 250 and 380 HV. Compared to direct current conditions pure nickel films from an acidic sulfamate bath exhibited a hardness between 330 and 360 HV [11]. Thus, in accordance with the literature [42,44] it appears that both PP and PRP conditions have only little impact on the hardness of nickel coatings from the sulfamate bath. The dependence of the microhardness of pure copper and copper alumina composites on the pulse duty cycle is shown in Fig. 10a. The microhardness values for the copper films range from 45 for pure copper to 85 HV for composite films (Fig. 10a). These hardness values are in good agreement with literature [45] where the hardness of copper films plated



Fig. 7. Cross-sectional scanning electron micrographs of pure copper and composite films deposited by PP deposition techniques at $\theta = 67\%$, f = 1.67 Hz, $i_P = 10$ A dm⁻². (a) Pure copper and (b) composite film, 10 g L^{-1} Al₂O₃ in the electrolyte.



10 µm

Fig. 8. Cross-sectional scanning electron micrographs of pure copper and composite films deposited by PRP deposition techniques at $i_P = 5 \text{ A dm}^{-2}$, $t_{on} = 50 \text{ ms}$ and $i_{an} = 1 \text{ A dm}^{-2}$, $t_{rev} = 20 \text{ ms}$. (a) Pure copper and (b) composite film, $10 \text{ g L}^{-1} \text{ Al}_2 \text{ O}_3$ in the electrolyte.

from an acidic sulfate bath is reported to be in the range from 50 to 105 HV. Furthermore, the hardness of the PP and PRP films is comparable to our previous results of copper films plated under DC conditions [13].

The hardness of metal films as well as MMCs is known to be related to the structure of the matrix and the amount and distribution of the reinforcing metal oxides particles [9,11,13]. The results shown in Fig. 10a indicate that the shorter the pulse off-time (i.e. the higher the duty cycle) the higher the hardness of the copper coatings. At the first glance, it might be difficult to rationalize this finding. Note that the amount of codeposited particles in the copper layer decreases with increasing duty cycle (Fig. 1). Hence, the enhanced hardness of the composites is not directly related to the absolute amount of particle incorporation. However, in accordance with our results from DC deposition [13] the effect of nanoparticle codeposition on the structure of the copper films has to be considered. The structure of the copper film changes due to a variation of the deposition parameters (Figs. 7 and 8). At low peak current densities the average grain size of pure copper films is known to decrease with a relative increase of the pulse pause [24]. Hence, the dependence of the hardness of copper coatings on the duty cycle (Fig. 10a) is probably related to microstructure of the copper films.

In accordance with the literature [26] the microhardness of pure nickel films and nanocomposites tends to increase with decreasing duty cycle (Fig. 10b). These results are in good agreement with the effects of duty cycle on the surface morphology of the coatings (Fig. 6). It is well known that the hardness of nickel films plated from the acidic sulfamate bath under DC conditions increases with decreasing plating current density [45]. In PP experiments the average plating current density (Eq. (1)) increases with decreasing duty cycle and increasing pulse frequency. Hence, the improved hardness of the nickel films due to a variation of the plating parameters (Fig. 10b) can be explained by the change of the average current density, which is in good agreement with the results of DC plating [45]. A lower duty cycle means a relatively longer pulse pause that leads to an enhanced incorporation of alumina particles within the metal matrix (Figs. 1 and 2).

Finally, the hardness of the copper and nickel nanocomposites is only slightly affected by the absolute amount of incorporated alumina particles. The main parameter governing the hardness of the coatings is the structure of the metal matrix that is principally influenced by the average plating current density. As a result of the particle incorporation, the microstructure of metal films plated from acidic electrolytes changes from the FT-type (Figs.



Fig. 9. Cross-sectional scanning electron micrographs of coatings prepared by PP at $\theta = 67\%$, f = 1.67 Hz, $i_p = 10$ A dm⁻². (a) Pure nickel and (b) nickel alumina composite deposited from an electrolyte containing 10 g L⁻¹ Al₂O₃.



Fig. 10. Correlation between the vickers microhardness of pure metal and nanocomposite films and the pulse duty cycle at a plating current density of 10 A dm^{-2} ; (\blacksquare) 0 g L^{-1} ; (\blacksquare) 1 g L^{-1} ; (\blacksquare) 1 g L^{-1} ; (\blacksquare) 10 g L^{-1} . (a) Copper and (b) nickel.

7a, 8a and 9a) to the UD-type (Figs. 7b, 8b and 9b), which is known to significantly improve the hardness of the coating [11,13].

4. Summary

Copper and nickel alumina nanocomposites have been obtained by means of DC plating, pulse plating (PP) and pulse reverse plating (PRP). The percentage of alumina particles in the metal coating varied from 0 to 5.6 wt% depending on the metal matrix and the deposition technique. A maximum incorporation of about 5.6 wt% alumina was obtained in the case of PP Cu–Al₂O₃ composite at a peak current density of 10 A dm^{-1} , a duty cyle of 20%, a pulse frequency of 8 Hz and a particle content of $10 \,\mathrm{g} \,\mathrm{L}^{-1}$ alumina in the electrolyte. The alumina content in the metal matrix increased with the particle loading of the electrolyte, pulse frequency and decreasing duty cycle. Although the particle content of the deposits prepared by PRP was higher compared to those of DC plating, the absolute amount of particle incorporation in a copper matrix was only slightly affected by a change in the PRP working conditions. In the case of Ni-Al₂O₃ PRP seems to be a useful method to increase the particle inclusion almost two times in comparison to DC plating.

The microhardness of the pure metal and the nanocomposite films was characterized as a function of the interdependent PP working conditions such as duty cycle and pulse frequency. Similar to the results found in the case of DC deposition of metal matrix nanocomposites, it has been shown that the hardness of the composite films prepared by PP and PRP mainly depends on the microstructure of the metal matrix.

In general, both PP and PRP are proved to be advantageous for controlling and improving both the particle content and the properties of metal matrix nanocomposites.

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