Novel post treatment of nano-particle reinforced metallic coatings

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ABSTRACT

Electrochemical co-deposition of metallic coatings with a second phase material have been widely applied in industry to improve the properties of coatings. A variety of hard oxide, carbide, nitride, and ceramic nanoparticles have been successfully co-deposited within different metal matrices. These nano-composite coatings are generally prepared by dispersing the secondary phase particles as a powder in a plating bath by means of vigorous agitation; however, this process is not simple to industrialize and presents an environmental hazard if nano materials become airborne.

Patented Dopant™ technology from Cirrus Materials Science offers a means to create high value nano-composite coatings without the implementation and process drawbacks of powder mixing. Cirrus Dopant™ is an aqueous form of precursor nano-structured material that supports in-situ creation of nanoparticles during the plating process. This technology is applicable to commercial baths for a large variety of electrolytic and electroless coatings.

The improved mechanical properties of nano-reinforced coatings were generally created by the refined microstructure and dispersion strengthening engendered by the presence of the nano-particle. To achieve optimum results, a customised Dopant™ formulation and dosing regime is required for each bath. Recently, Cirrus discovered that a novel post-treatment process for coatings reinforced with Cirrus Dopant™ improves the hardness and ductility of the coating by >40%. To date, all the coatings created using Cirrus Dopant have shown improved mechanical properties after post treatment. This paper discusses the process and latest results for nano-doping commercially relevant coating baths.

Keywords: nano-composite coatings, dopant, electroplating, nanoparticles, dispersion strengthening

1 INTRODUCTION

Composite coatings are widely applied in industry as surface finishing to improve their mechanical properties and corrosion resistance. Electroplating or electroless plating is a common technique to produce composite coatings due to low cost and simple operation. Often coatings are subject to stress such as tensile stress or compressive stress during deposition, generally as a function of the bath chemistry and deposition parameters [1]. To eliminate such stress, coatings are frequently subject to post deposition treatment, such as heat treatment, which generally increase the grain size and reduce the hardness of the coatings, while lowering the internal stress in the deposit.

The presence of a secondary phase in the coating may change the stress accumulation characteristics of the coating. This in turn affects the stress related properties of the coating system. Cirrus has observed both experimental and real-world applied coating performance which significantly exceeds expectations when incorporating Cirrus dopant to form a doped coating followed by post treatment at high temperature. Here we report our investigation of certain mechanisms which impact the performance of composite ceramic coating systems prepared with Cirrus Dopant, including externally applied stress and/or heat treatment. We find that doped coatings generally respond differently to both externally applied stress and heat treatment regimes than comparable undoped coatings. Furthermore these behaviours are sufficiently predictable that coating post treatment systems that improve both the hardness and wear resistance of composite coatings, while substantially maintaining the ductility of the coating system, may be developed.

2 METHODLOGY

The study reported here involved three coating types and three substrates. The substrates were copper, copper beryllium, and mild steel. The coatings applied were electroplated nickel, electroplated gold, and electroless nickel-phosphorous. Two aqueous dopant variations were used, the first was a alumina dopant which typically created particles in the order of 40-60 nm in the coating matrix. The second was a zirconia dopant where particle sizes are typically less than 10 nm. Pre-treatment of the susbtrates followed commercial practise and involved multiple steps as outlined in Table 1.

A simple oven with the temperature controlled for repeatability using a thermocouple was used for post treatment. The coating hardness was measured by using a DuraScan 70 G5 hardness tester. Wear testing was conducted using a Nanovea micro-tribometer where an 6mm diameter alumina ball acted as a friction counter ball. The load, speed and duration were selected according to the coating. In the case of thin nickel or gold coatings hardness and wear testing were replaced by nano-indentation using Hysitron TI 950 TriboIndenter. The phase structure coatings was characterized by Ultima IV, Rigaku X-ray diffractometer (XRD).

Table 1: Substrate preparation regime.

Cu Substrate or Cu-Be Substrate		
Chemicals	**Process**	**Time**
Activax	Immersion	5 min
	Cathodic	1 min
	Anodic	10s
118 Cyanide	Cathodic	30s
5% H_2SO_4	Activation	1 min
Mild Steel Substrate		
10% HCl	Remove ZnO	30s-1 min
Alkaline-de-	Cathodic	1 min
ruster	Anodic	1 min
10% H_2SO_4	Activation	30s

3 RESULT AND DISCUSSIONS

3.1 Effects of post-treatment on electroless Ni coatings

Table 2**Error! Not a valid bookmark self-reference.** shows some early results obtained when heating doped and undoped electroless nickel coatings to low temperatures, here the samples were heated to 210℃ for four hours. As expected the hardness of an undoped electroless nickel coating changes very little as the treatment temperature is below the level at which Ni_3P particles will precipitate. In contrast the doped coating underwent significant hardening with the degreee of hardening dependant on the the substrate.

Table 2: Low temperature heating of electroless nickel coatings.

Coatings	Substrate	Hardness	
		As-Plated	Post-Curing Process
Electroless Ni	Cu-Be	601.00±8.70	614.86±15.83
Electroless Ni with Al Dopant™	Cu-Be	752.20±13.92	901.40±15.22
Electroless Ni with Al Dopant™	Mild Steel	610.43±15.57	730.00±11.85

Heat-treatment is commonly performed after electroless plating to enhance the hardness and wear resistance of the deposit, especially for amorpohous coatings. High phosphorous electroless Ni coatings become crystalline during heat treatment due to the precipitation of hard intermetallic phase, for example Ni_3P particles. Precipitation of second phases leads to increased hardness as the precipitated particles act as barriers to dislocation movements [2,3]. However, beyond an optimum level, further aging or heat treatment will begin to decrease the hardness due to grain growth, coarsening of the Ni matrix and equilibrium Ni_3P precipitation [4]. Thus, the degree of hardening greatly depends on the amount of phosphorous, the tempearature and duration of heating. For low phosphorous coatings, optimum crystalinity occurs at 400℃ while for high phosphorous it may happen at 330-360℃. In general, the maximum hardness is usually obtained after heat treatmet at 400℃ for 1h [5]. Theoretically, electroless Ni-P nanocomposite coatings could improve the mechanical properties when the coating is heat treated at 400℃ for 1h; however it's worth noting the resultant structural change and shrinkage of the Ni-P matrix may not be accommodated by the secondary phase nanoparticles, producing cracking that decreases the corrosion resistance significantly [6]. In this research, the heat treatment was performed at 210℃ for a relatively short period, which was found to not only improve the hardness but also prevent any cracking.

Thermal stress will be generated when a coating and substrate are at a temperature that is significantly different from the temperature during deposition. This stress is a result of the difference in thermal expansion coefficients between the coating and the substrate [7]. Table 3 provides thermal expansion coefficeint data for several coatings and/or typical substrate materials. When a Ni or NiP coating is deposited on copper substrate and heated to 210℃ for a certain period, a tensile stress is generated in the coating material. On the other hand, if the Ni coating is deposited on mild steel a compressive stress is generated. Two factors appear to explain the reduced impact of post-curing on mild steel noted in Table 2: development of compressive rather than tensile stress, and a lower overall stress level, perhaps only slightly above the elastic limit.

Table 3: Thermal expansion coefficient for different materials.

Materials	Linear Temperature Expansion Coefficient, α (10^{-6} m/mK)
Copper	16-16.7
Nickel	13
Steel	11-12.5

3.2 Effects of post-treatment on electroplating coatings

Table 4 shows the reduced modulus and hardness of doped and undoped Ni and Ni/Au duplex coatings on a Cu susbstrate. The thicknesses of Ni and Au are 2.5 and 0.87 µm, respectively. All coatings were subjected to post-treatment at 200℃ for 2 hours. Hardness was measured using standard quasi-static load-controlled indents with 5000 µN maximum load, 5s loading (1000 µN/s loading rate), 2s holding, and 5s unloading (1000 µN/s unloading rate). 3×3 array indents at 3 different locations (27 indents) were completed for each sample.

It can be clearly seen that doped nickel is significantly harder than undoped nickel. In the case of the gold coatings the doped gold shows a hardness increase, however care must be taken in interpreting the results as the nickel underlayer has potential to influence the measurements. In all cases the reduced modulus for doped coatings is significantly higher than that for undoped coatings which may improve wear resistance of the surface material.

Table 4: Reduced modulus and hardness of doped and undoped Ni or Ni/Au duplex coatings.

Coatings	Reduced Modulus, Er (GPa)	Hardness, H (GPa)
Ni+Zr Dopant™	158.3±7.6	8.75±0.6
Ni+Zr Dopant™/Au +Zr Dopant™	143.4±11.7	3.90±0.5
Ni Undoped	82.0±5.2	6.27±0.5
Ni Undoped/ Au Undoped	62.2±2.1	2.81±0.1

To evaluate wear, 3 nano scratches were performed on each sample, with each scratch separated by 5 µm. Each 10 µm long scratch was made using a 1 µm radius diamond conical tip, a 5000 µN maximum axial load, and a scratch speed of about 0.67 µm/s. Figure 1 shows the comparitive scratches for doped and undoped Ni or Ni/Au duplex coatings. The gold coatings show significantly lower scratch resistance, as evidenced by the larger scratches made using the same load. This is consistent with the lower hardness of gold compared to nickel. Dopant slightly reduces both the scratch width and CoF in all coatings. The uniformity of the doped coatings is much better, as evidenced by the very low measured standard deviation as shown in Table 5.

Table 5: Average of COF coatings of different coatings.

Coatings	COF
Ni+Zr Dopant™	0.251±0.002
Ni+Zr Dopant™/Au +Zr Dopant™	0.419±0.003
Ni Undoped	0.256±0.008
Ni Undoped + Au Undoped	0.444±0.007

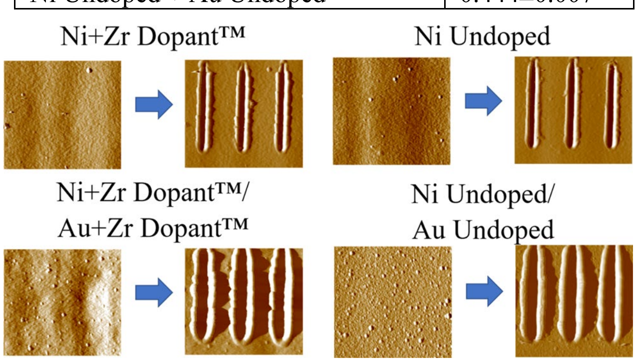

Figure 1: Nanoscratch on doped and undoped Ni or Ni/Au duplex coatings.

3.3 Applications of post-treatment of doped-coated coatings

Hot runner injection moulding tips are one of the components used in plastic injection molding. The melt polymer, or liquid plastic, is transported through a hot runner, and injected into a mould through the tip. Hot runner greatly increases the efficiency of injection moulding due to their ability to reduce material use and increase productivity; however, the main challenge is maintaining a flat thermal profile [8]. This is accomploshed by using a copper-beryllium (Cu-Be) high thermal conductivity substrate and thin, wear resistant coatings.

In order to obtain improved wear resistance, Cirrus modified the current commercial products from a standard high-phosphorus electroless nickel (HPEN) to a low-phosphorous doped electroless nickel (LPEN) coating using alumina dopant.

Figure 2 shows wear performance of the hot runner tips after accelerated wear using glass reinforced plastic on a 150-ton Arburg machine at a processing temperature of 240°C. An improved (doped) Ni tip (Fig. 2b and 2d) and a standard Ni tip were tested parellel to evaluate any performance differences. Identical temperature and pressure was maintained on both tips during testing. The standard Ni tip exhibited observable wear after 400 cycles while there is no visible wear for the doped Ni tip. A further 800 cycles of injection was performed, where the standard Ni tip is worn to the copper-beryllium substrate which limited for further testing. The doped tips were tested to over 4000 cycles without observable wear.

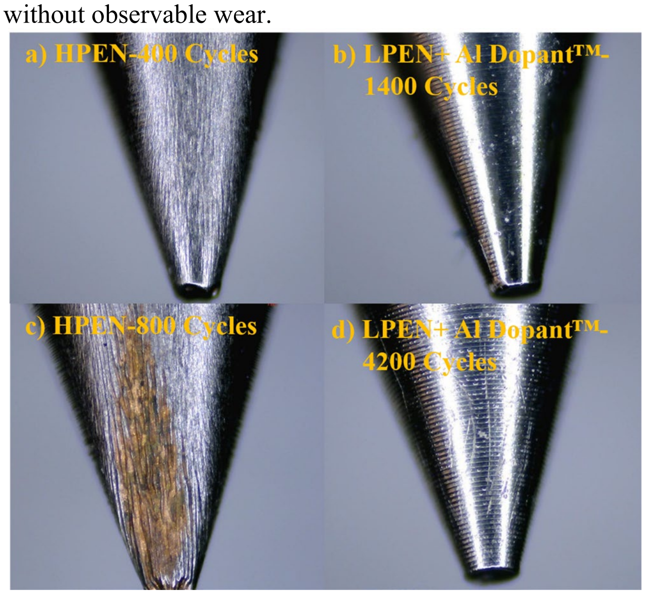

Figure 2: Appearance of hot runner tip after testing in an injection molding.

To better understand the the wear resistance results for the hot runner tips. Cu-Be discs coated under the same conditions were evaluated. These samples were also heat treated in an oven at 210°C for 4h. Figure 3 shows the XRD spectra for HPEN and LPEN+Al Dopant samples as-plated and after heat-treatment at 210°C for 4h. Clearly, no intermetallic formation can be observed during heat treatment, attributably to the low processing temperature where crystallization will not occur [9].

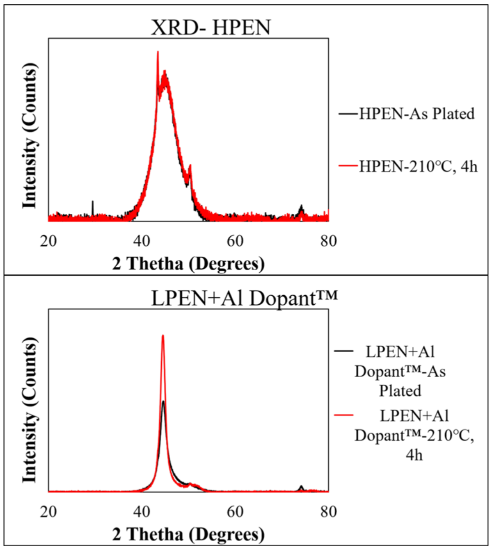

Figure 3: XRD of as-plated and post treatment for HPEN and LPEN+Al Dopant.

A wear test was performed with an applied load of 2N and duration of 15 min using an Al_2O_3 6mm ball. Figure 4 compares the coefficient of friction (COF) of both coatings, where a lower COF for the doped coating can be observed compared to the standard Ni coating.

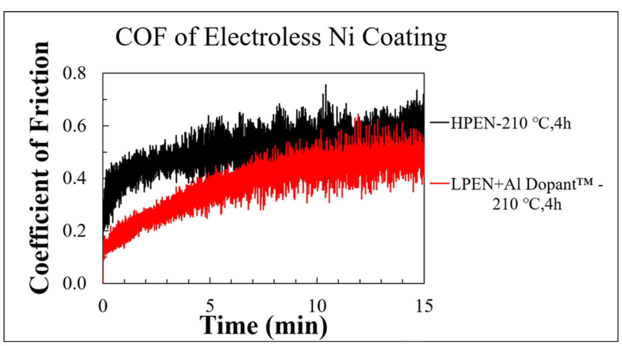

Figure 4: Comparison coefficent of friction of standard Ni and doped Ni plated on Cu-Be disc.

Wear resistance of a coating is strongly dependent on factors such as hardness, surface roughness and microstructure, which for nano-composite materials includes the volume of particles in dispersion and the inter-particle distance. Under identical wear test conditions, the wear volume is proportional to the friction coefficient and inversely proportional to the hardness of the contact surface [10]. Thus, doped Ni tips provide outstanding wear resistance due to a higher hardness and a lower COF compared to standard Ni tips.

4 CONCLUSIONS

A heat treatment regime was explored to enhance nanocomposite coatings for the first time. The heat treatment was only applied at low temperature and for a short period of time to avoid any grain growth or precipitation of intermetallics in alloy plating. The hardness and wear resistance of low temperature treated coatings was significantly improved compared to both undoped coatings and as-plated doped coatings. In addition, post heat treatment of the doped-coated sample also could decrease the reduced modulus. Such post heat-treatment may open up new applcations in synthesizing nano composite coatings especially those coatings required to operate at below 300°C, and one such application is hot runner tips for the injection molding industry.

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