Applications of Nano-Scale Cirrus Dopant™ to Improve Existing Coatings

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Abstract

The use of ceramic nano-powders to create composite coatings is well known but is neither simple to industrialize nor environmentally friendly. Patented Cirrus Dopant™ technology from Cirrus Materials Science offers the performance advantages of nano-composite coatings without the implementation and process drawbacks. Cirrus Dopant™ technology is applicable to commercial baths for a large variety of electrolytic and electroless deposited coatings including Ni, Ni-P, Ni-B, Co-P, Au, Ag, Sn, and Zn-Ni. Successful application of the technology simply requires optimization of a specialized Dopant™ to the bath. This paper discusses the process and results for nano-doping commercially important coating baths. Copyright © VBRI Press.

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Introduction

Coatings are typically applied to the surface of manufacture components to improve the durability of the surfaces and products by increasing their resistance to wear, corrosion, erosion, fatigue, or fracture [**1**]. Numerous protective coating techniques have been developed such as electroplating, electroless plating, plasma thermal spray, hot dipping and vapour deposition methods [**2, 3**]. Among these methods, electroplating is a cost-effective approach for industrial applications due to its simple equipment and process requirements, low cost, ambient atmospheric conditions, and excellent reproducibility.

Advance nano-composite coatings and materials have attracted a great deal of interest in surface finishing, due to their superior mechanical properties when compared to traditional coatings. A variety of hard oxide, carbide, nitride, and ceramic nanoparticles have been successfully co-deposited with different metal matrices [**4, 5**].

The creation of nano-composite costing with ceramic nano-powders is neither simple to industrialize nor environmentally friendly. Patented Cirrus Dopant™ technology from Cirrus Materials Science offers the performance advantages of nano-composite coatings without the implementation and process drawbacks. Cirrus Dopant™ technology is applicable to commercial baths for a large variety of electrolytic and electroless deposited coatings including Ni, Ni-P, Ni-B, Co-P, Au, Ag, Sn, and Zn-Ni. Successful application of the technology simply requires optimization of the specialized Cirrus Dopant™ to the bath. This paper discusses the process and latest results for nano-doping in some commercially important coating baths.

Experimental

Electroplating using Cirrus Dopant™, in practice, is little different from normal electroplating. The dopant operates as an additional additive to the bath.

When the dopant, which may include long chain proto-nanoparticles, is added to the plating electrolyte, these proto-particles form nanoparticles of a "desirable size". The formation process is dependent on the pH of the bath, the type of dopant, and the ion species in the bath; however, the "desirable size" is related to the type of coating to be plated. In most applications, the dopant particle size is controlled to stabilize between 5 nm and 40 nm.

As nanoparticles form in the bath, they are stabilized by the surrounding hydrate metal ions. Since we can control dopant characteristics for a given bath chemistry, the process may be optimized by adapting the particle surface change to an appropriate positive or negative value. The stabilization process prevents significant agglomeration of the nanoparticles and ensures that they are uniformly distributed throughout the bath and thus the coating.

During plating, depending on the plating bath dynamics, a combination of mechanisms, including electrophoresis, diffusion, and convection, transport the particle complexes to the cathode surface. At the cathode the particles are adsorbed, as their associated metal ion cloud is reduced, and incorporated into the coating. By ensuring a uniform dispersion of particles in the bath, and a uniform rate of transport to the cathode, uniform particle incorporation into the coating surface can be achieved.

In this paper, most experimental plating bath solutions were commercially sourced. Cirrus Dopant was prepared substantially using the methods described in our previous published papers [**6-8**].

High resolution transmission electron microscopy (FEI Tecnai G2 F20, 200 kV) was used to investigate the dopant deposits in the coating. For the TEM sample preparation, the coating with a thickness of ~10 µm was first deposited on a stainless-steel substrate. The coating was then peeled off and thinned using a low angle ion beam milling system (Fischione Instrument Model 1010) to obtain proper sample for TEM observations. The microstructure and surface morphology of coatings were also investigated by environmental scanning electron microscopy (ESEM).

The wear property of coatings was tested using a NANOVEA tribometer, with a friction counterpart of a 6 mm diameter ruby ball. A load of 2 N, sliding speed of 100 mm/s and duration of 20 min were used at room temperature. The width of wear track was measured under an optical microscope.

The corrosion tests were carried out at room temperature (25 ^{o}C) using a standard flat cell with three-electrode system: platinum mesh as auxiliary, saturated calomel electrode (SCE) as reference and coated specimen as working electrode. The corrosion current density and corrosion potential were determined based on Tafel's extrapolation. The exposed surface area of all samples was 1 cm^2.

Anti-microbial property tests were performed on the moist surface of nickel coatings. The test method adopted is based on the Japanese Industrial Standard (JIS: Z2801:2000) and America Society for Testing and Materials (ASTM E2180-07) [**9, 10**]. Tests were performed in triplicate and the results reported are the geometric mean (logX) of the number of bacterial colonies from test and control samples using the following equation:

$$\text{Geometric mean} \quad = \frac{(\log X_1 + \log X_2 + \log X_3)}{3}$$

where X_1, X_2 and X_3 is the number of counted bacterial after incubation period.

Results and discussion

Effects of dopant on microstructure

Fig. 1 shows the bright field TEM image and HRTEM of Cirrus Dopant™ Ti particles in a silver coating plated from a commercial cyanide silver bath solution. Multiple spherical 20 nm nano-particles appear as white particles distributed uniformly along the silver grain boundaries. The nanoscale probe EDX analysis indicates the nano-particles contain Ti, while HRTEM show that that nano-particles have an amorphous microstructure as shown in right image from **Fig. 1**. These nano-particles not only provide dispersion strengthening, but also increase the number of nucleation sites which contribute to grain refinement in the coating.

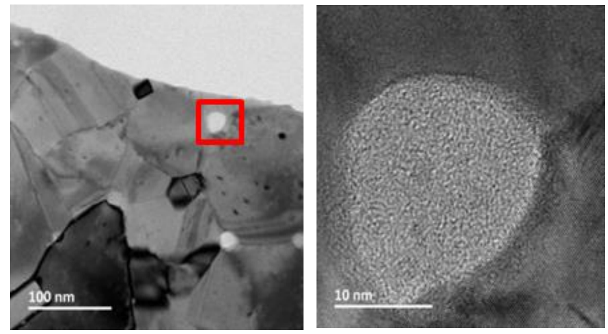

Fig. 1. Bright field TEM image and HRTEM image of Ti Cirrus Dopant™ in silver coating.

Effects of dopant on mechanical properties

Cirrus Dopant™ has been well studied with different coatings such as Ni, Ni-P, Ni-B, Ag, Au-Ni, Cu, Zn-Ni, etc. Typically, the introduction of a dopant produces a 15% - 60% hardness improvement, depending on coating, dopant, and bath formulation.

For example, the measured Vickers hardness of a conventional Ni coating on mild steel was ~320 $HV_{0.1}$. When the reducing agent DMAB was added to produce Ni-B, the hardness of Ni-B improved 35% to ~550 $HV_{0.1}$. However, the addition of Cirrus Ti Dopant™ increased the hardness by a further 60% to over 1000 Vickers.

It is interesting to note that while the improvement of hardness may be attributed to the combination of grain refinement and dispersion strengthening; the latter is more important, as the grain size change is relatively small. An appropriate dopant added to a plating bath results in a uniformly distributed co-deposition of nano-particles in the coating. The dispersed nanoparticles prevent dislocation slip, and thus increase the hardness of a coating. When excessive dopant is added, the stabilization mechanism is overloaded, and nanoparticles tend to agglomerate. Depositing agglomerated nanoparticles produces a porous coating structure at the grain boundaries, minimizing any the dispersion strengthening effect and degrading the mechanical properties. While the grain refinement mechanism is still present, the porous microstructure will significantly reduce the hardness compared to a compact coating. However, a number of researchers have suggested that the addition of surfactant minimizes the agglomeration effect [**11**]. Thus, the addition of surfactant could potentially improve the dopant performance at higher levels of doping.

In the following example, wear tests were performed using a Nanovea Tribometer on a Cu coating and Cirrus Al doped copper composite coating. All the wear surfaces were observed under optical microscope and are shown in **Fig. 2**. The wear volume losses were calculated and plotted against various concentrations of Al dopant in **Fig. 3**.

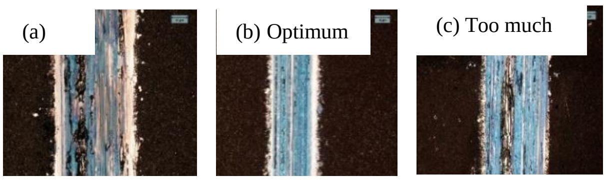

Fig. 2. Worn surfaces of Cu coating with (a) no dopant, (b) optimum dopant and (c) too much dopant.

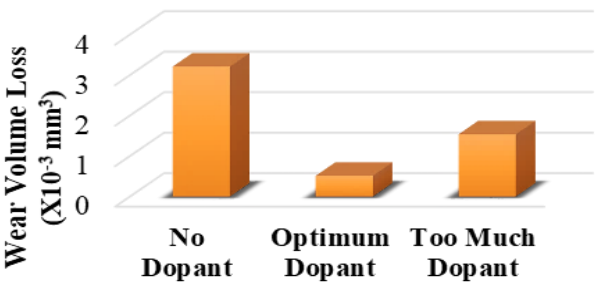

Fig. 3. Wear Volume loss of Cu and Cirrus Al doped Cu composite coating.

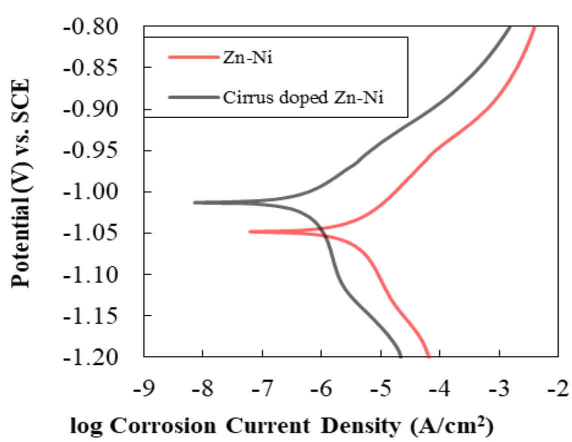

Fig. 4. Tafel plots of Zn-Ni and Cirrus doped Zn-Ni composite coatings in 3.5 wt.% NaCl solution.

It can be clearly seen that the quantity of dopant added plays an important role in improving the wear resistance of plated copper. A wider wear track and many plough lines were observed on the worn surface of pure Cu coating. In contrast, the wear tracks on the correctly Al doped Cu coating were much narrower and the plough lines were shallower compared with that of the pure Cu coating. By using the correct amount of dopant, the wear volume loss was reduced by up to 90%. Conversely, over-doped coatings perform less well, when compared to the optimum dopant level, because of the porous microstructure created.

Effects of dopant in corrosion resistance

Fig. 4 shows the Tafel plots of both Zn-Ni and Cirrus Al doped Zn-Ni coatings in a 3.5 wt. % NaCl solution. The corresponding electrochemical parameters extracted from the plots are summarized in **Table 1**. These results show that with the addition of Cirrus Al dopant, the corrosion potential for the coating shifts in a positive direction, showing a general tendency towards a decrease in the corrosion current density.

Table 1. Corrosion Parameters extracted from Tafel plots.

Sample	Ecorr. VS. SCE (V)	Icorr. (μA/cm^2)
Zn-Ni	-1.048	6
Cirrus Al doped Zn-Ni	-1.013	0.8

The improvement of the corrosion resistance of Cirrus Al doped Zn-Ni is mainly due to the dopant lowering the coating internal stress and reducing instances of through-cracking. A similar trend was noted by Sheu *et al.* [**12**]. The authors reported that incorporation of Al_2O_3 particles into a trivalent chrome coating reduces the corrosion current density by about one order of magnitude compared to that of pure trivalent chrome coating. The Al_2O_3 particles not only reduced the formation of cracks, but also have intrinsic high corrosion resistance.

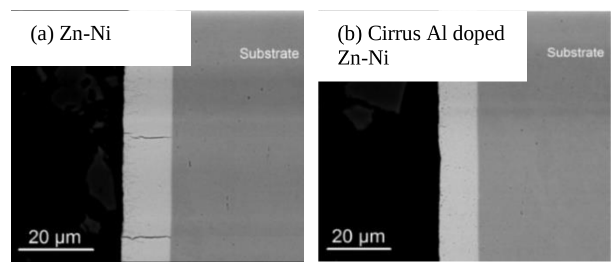

Fig. 5. Cross-section images for (a) Zn-Ni, (b) Al Cirrus doped Zn-Ni coating.

Fig. 5 shows the cross-section images of a Zn-Ni coating and a doped Al_2O_3 Zn-Ni alloy coating. The results demonstrate that the typical Zn-Ni coating contains through microcracks to the substrate caused by the build-up of internal stress, while a Cirrus Al_2O_3 doped Zn-Ni, coated under identical conditions, was crack free. This reflects that the Cirrus Al_2O_3 doped coating is more compact and stress free when compared to the Zn-Ni coating.

Effects of dopant in anti-microbial properties

Fig. 6 shows bactericidal properties of Ni coating and Cirrus Ti doped Ni coating. The control is an uncoated mild steel in this experiment. The reduction of E. coli quantities was observed within 5 hours. Cirrus Ti doped Ni coating showed a better antimicrobial capability than the Ni coating. TiO_2 is well known it possesses antibacterial functions by its photocatalytic properties [**13**]. TiO_2 could produce highly reactive hydroxyl radicals and electron that react with oxygen vacancies to form superoxide ions. These superoxide ions thus oxidize the organic cell and destroy the micro-organism [**14**]. Thus, Ti Cirrus doped Ni coating performed better anti-microbial properties than pure Ni coating.

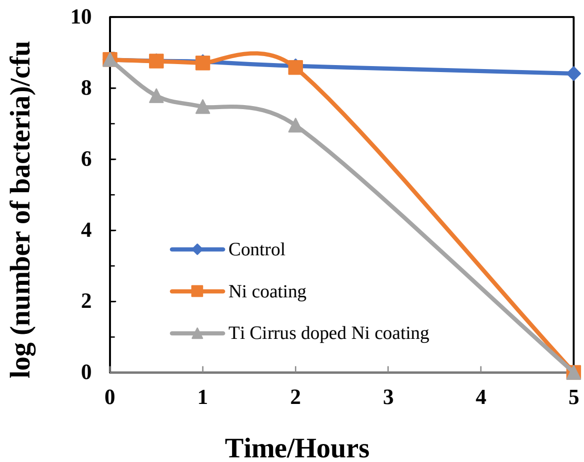

Fig. 6. Five-hour bactericidal performance.

Conclusion

In summary, Cirrus Dopant is an innovation that offers the ability to deposit a wide variety of nano-composite coatings without directly handling the nanoparticles. It works as a liquid additive to the plating bath, with no requirement to make any significant change in existing plating process or equipment. Once Cirrus Dopant™ is added to the plating bath, the resulting nano-composite coating will out-perform regular coatings in terms of mechanical properties and corrosion, while maintaining the desirable characteristics of original coating, such as conductivity, and appearance. In industrial use, the dopant is applicable to a wide variety of coatings, substrates, and surface finishing applications.

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