The use 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 the specialized Dopant™ to the bath. This paper discusses the process and results for nano-doping commercially important coating baths.

Introduction

Coatings are widely applied on the surface of products to improve the durability of the materials 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 physical 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.

Currently, nano-composite coatings have attracted a great deal of interest in surface finishing compared to the conventional composite coatings due to their superior mechanical properties. A variety of hard oxides, carbides, nitrides, and ceramic nanoparticles have been successfully co-deposited with different metal matrices [4, 5, 6].

Generally, nano-composite coatings are synthesized by adding solid nanoparticles directly to the electroplating baths and maintaining the particles in suspension during processing, so that the particles are incorporated into the deposited metal matrix [7]. The incorporation and the uniform dispersion of nanoparticles in the deposit are critical as they provide the superior performance achieved by precipitation strengthening. To attain a good dispersion, processes such as ultrasonic vibration, bubble injection, air injection or coating the particles with surfactants are used to assist maintaining the critical particle dispersion and preventing agglomeration. Despite these techniques it is difficult to maintain the necessary distribution and create a homogeneous composite coating matrix due to the large particle surface area and tendency to agglomerate [8]. Thus, the challenge remains to produce highly dispersed nanoparticles in a composite, electroplated coating that will provide superior mechanical properties in industrial applications.

To answer this challenge, we have developed Cirrus Dopant™ technology, which is an additive to standard plating bath solutions. The dopant is a liquid, containing proto nanoparticles. Since the dopant contains nanoparticles in liquid form, it minimises agglomeration when combining with a plating solution. During electroplating, the nanoparticles co-deposit uniformly throughout the plating process, creating a homogenous composite coating. The proto-nanoparticles produced by the dopant in the plating bath are amorphous rather than ceramic crystals, and will remain in suspension once stabilised.

Dopant Science

Electroplating using Cirrus Dopant™ in practise is little changed from regular electroplating. The dopant is used as an additional additive to the bath.

When the dopant, which includes long chain proto-nanoparticles, is added to the plating electrolyte, these proto-particles form new 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, this "desirable size" is related to the type of coating to be plated. In most applications, the dopant particle size is controlled to stabilise between 5 nm and 40 nm.

As nanoparticles form in the bath, they are stabilised by the surrounding hydrate metal ions. Since we can control dopant parameters for a given bath type, this process can be optimised by adapting the surface change of the particle between appropriate positive or negative values. The stabilisation process prevents significant agglomeration of the nanoparticles and ensures that they are uniformly distributed throughout the bath and thus the coating.

During plating, and depending on the type of plating bath, under the various effects of electrophoresis, diffusion, and convection the particle complexes are transported to the cathode surface and adsorbed together with their metal ion cloud into the deposited 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 produced.

Effects of Dopants

Microstructure

Fig. 1 shows the bright field TEM image and HRTEM of Cirrus Dopant™ Ti particles in the 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 Fig. 1b. These nano-particles not only provide dispersion strengthening, but also increase the number of nucleation sites and producing grain refinement in the coating.

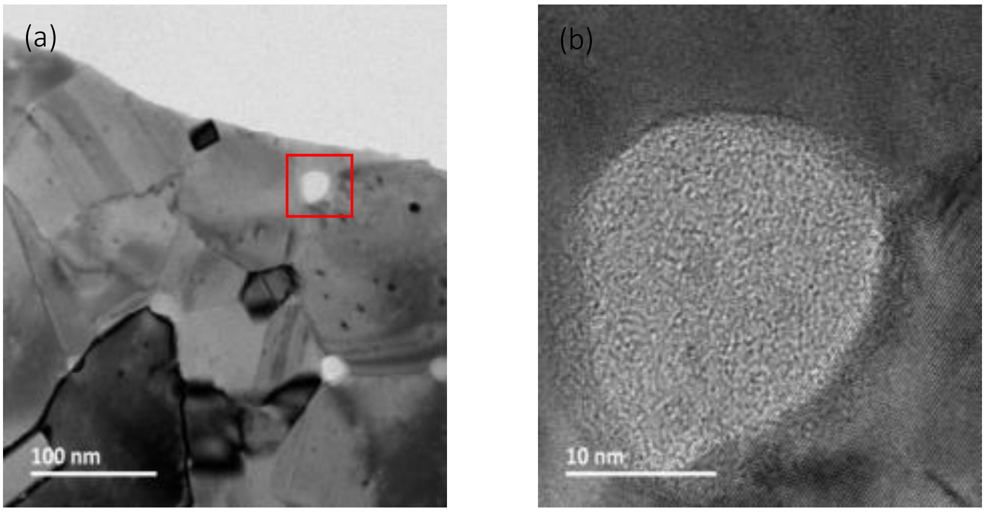


Figure 1: Bright field TEM image and HRTEM image of Ti Cirrus Dopant™ in silver coating.

Mechanical Properties

Cirrus Dopant™ has been well studied in 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 $HV_{0.1.}$ Finally, addition of Cirrus Ti Dopant™ increased the hardness a further 60% of over 1000 Vickers compared to the NiB coating.

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 change in grain size change is relatively small. When an appropriate dopant is added to a plating bath, the nanoparticles formed *in-situ* are uniformly co-deposited into the coatings. The uniformly dispersed nanoparticles prevent dislocation slip, and thus increase the hardness of a coating. When too much dopant is added, the stabilisation mechanism is overloaded and nanoparticles tend to agglomerate. This creates a porous structure at the grain boundaries, reducing the effect of dispersion strengthening and deteriorating the mechanical properties (even though the grain refinement mechanism is still present).

In the next 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 different concentration of Cirrus Al dopant in **Fig. 3**.

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 when 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% compared to a pure Cu coating. Conversely, over-doped coatings perform less well, compared to the optimum dopant level, as a result of the porous microstructure this creates.

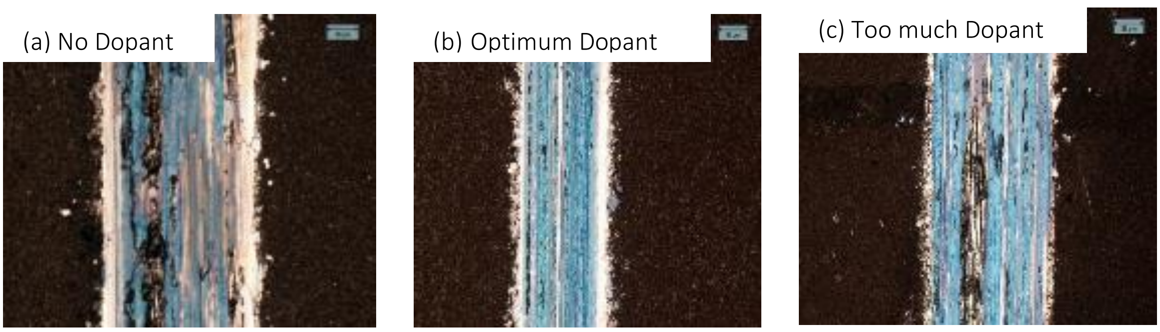


Figure 2: Worn surfaces of Cu coating with (a) no dopant, (b) optimum dopant and (c) too much dopant.

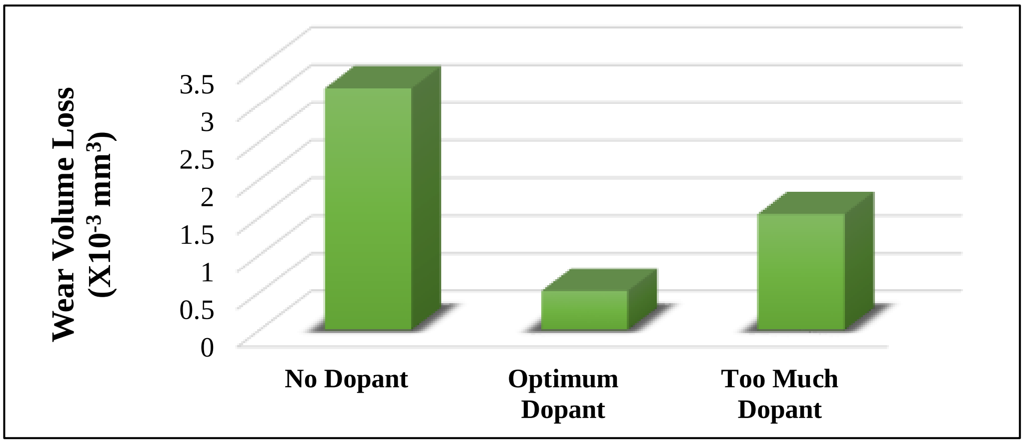


Figure 3: Wear Volume loss of Cu and Cirrus Al doped Cu composite coating

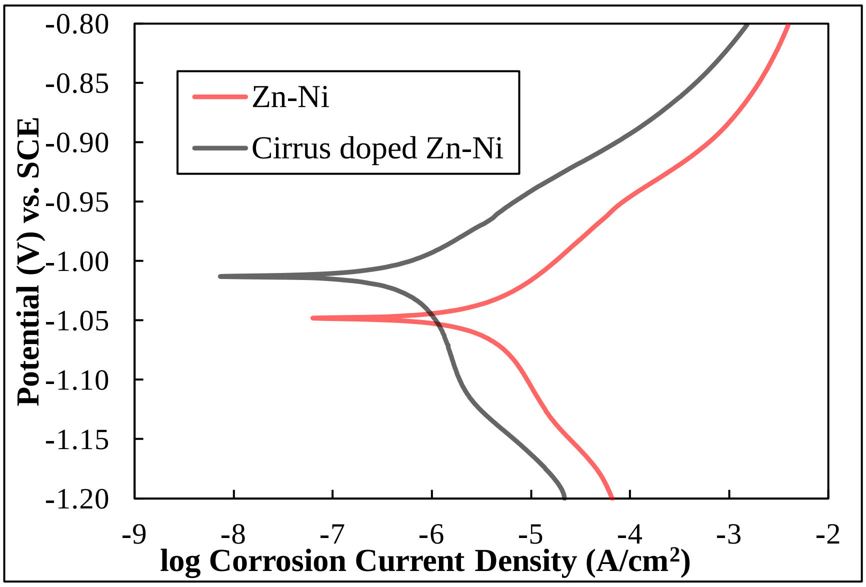


Figure 4: Tafel plots of Zn-Ni and Cirrus doped Zn-Ni composite coatings in 3.5 wt.% NaCl solution.

Corrosion Resistance

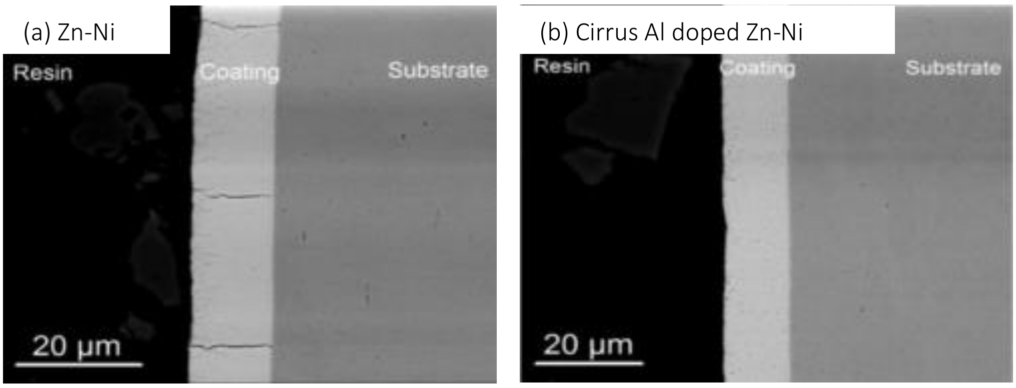
Fig. 4 shows the Tafel plots of Zn-Ni and Cirrus Al doped Zn-Ni coating in a 3.5 wt.% NaCl solution. The corresponding electrochemical parameters extracted from the plots are summarized in **Table 1**. These results show that with the addition of Cirrus Al dopant, the corrosion potential for the coating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

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

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

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



Anti-microbial Properties

Anti-microbial property tests were performed on the moist surface of coatings. The test method on the moist surface is based on the Japanese Industrial Standard (JIS: Z2801:2000) and America Society for Testing and Materials (ASTM E2180-07) [9, 10]. Fig. 6 shows bactericidal properties of Ni coating and Cirrus Ti doped Ni coating. The control is the substrate without coating on 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.

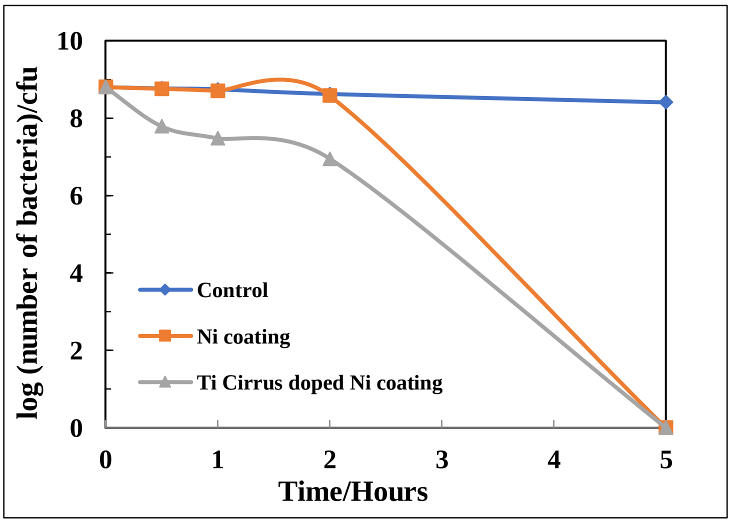


Figure 6: Five-hour bactericidal performance.

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, and there is 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 original coating functionality, 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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