Nanotechnology-Enabled Pretreatments Protect Lightweight Metal Alloys

The Pitch

NEI Corporation has developed a nanotechnology-based corrosion-resistant coating that will enable the widespread use of lightweight metal alloys in multiple industries. Structures and components made of lightweight metals, such as aluminum and magnesium, which have been used predominantly in aerospace applications, are now being increasingly considered in automotive and marine applications. Due to the propensity of lightweight metals to corrode rapidly, a highly corrosion-resistant system is used. In practice, a *pretreatment* is applied on the alloy surface, followed by several layers of organic coatings (e.g., epoxy, silicone alkyd, and urethane) which form the primer and topcoat. The pretreatment has both barrier and corrosion-inhibiting characteristics and is the key to providing corrosion protection, since the organic coatings are permeable to gas and water. Until now, chromate-based pretreatments (i.e., conversion coatings) have provided satisfactory performance. However, hexavalent chromium, which is released during production and use of coated components, as well as after disposal, is a known carcinogen. The U.S. Environmental Protection Agency (EPA) and Occupational Safety and Health Administration (OSHA) have severely curtailed the use of chromate-based materials. NEI Corporation has developed a nanocomposite pretreatment, which is chromate-free, and is designed to be a substitute for chromate-based conversion coatings used on lightweight metal alloy surfaces. The NEI pretreatment, which is essentially an inorganic–organic hybrid coating containing a dispersion of nanoparticles, is designed to protect lightweight metals through a combination of barrier and self-healing characteristics.

In addition to corrosion protection, the NEI pretreatment promotes adhesion of the metal surface to the organic primer layer by establishing a strong bond with the nascent oxide/hydroxide layer on the metal surface, and by providing functional groups as bonding sites for organic coatings applied over the pretreatment. This feature of the NEI pretreatment is particularly important in some applications (e.g., 6000 or 5000 series aluminum alloys) where the conversion or pretreatment coating step has been replaced by an abrasion step to promote the adhesion of primer with the metal surface: a 2–3 mil surface roughness is created by grit blasting. However, the abrasion step is not desired in the field because it creates hazardous metal dust, is labor intensive, and increases the total coating weight since the coating needs to fill the crevices on the surface.

The market for corrosion-protection pretreatment is both diverse and large. Just as an example, the annual cost of corrosion to the U.S. Department of Defense is estimated to be ~$20 billion. Primary applications for the NEI pretreatment include industrial, automotive, aerospace, maritime, and environmental/infrastructure uses. Lightweight metal alloys are fast emerging as attractive alternatives to steel for reducing the weight of components, specifically in automotive and maritime applications. Potential customers for the NEI coating include OEMs, such as the automotive manufacturers, as well as companies in the aftermarket and refinish business.

Table I: Cathode Current Density Values of AZ31B Magnesium Alloys with Different Pretreatment/Conversion Coatings.

Type of Surface Treatment	Current Density (mA/cm^2)
Blank	~20
Chromate (DOW 1 chemistry)	2.89
Hybrid Organic-Inorganic (NEI Pretreatment)	0.72
Hybrid Organic-Inorganic with Nanoparticles (NEI Pretreatment)	0.074

Note: Values are calculated from the cathodic polarization curves using the Gamry Echem software.

The Technology

NEI's nanocomposite pretreatment is a solution technology, and can be applied on metallic surfaces that have been cleaned either by commercial cleaners or organic solvents, such as acetone and isopropanol, using conventional coating technologies, including spraying and dipping. The coating is cured at a temperature lower than 100°C. The surface of the cured coating is smooth, and the thickness of the coating is between 1 μm and 5 μm depending upon the type of substrate, solids loading and nanoparticle concentration in the formulation, and coating processing parameters.

The adhesion as well as corrosion-protection properties are controlled by varying the nanoparticle loading and functionality. Cathodic polarization results demonstrate substantial improvement in the corrosion resistance of AZ31B magnesium alloy upon the application of the pretreatment. Addition of a small weight fraction of nanoparticles (<2 wt%) in the hybrid organic–inorganic coating decreased the corrosion current by an order of magni-

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tude. The corrosion current density values of panels from dc polarization studies are shown in Table I. The current density of the NEI pretreatment containing nanoparticles is two orders of magnitude lower than that of the chromate-treated sample.

The application of NEI pretreatment (with nanoparticles) imparted excellent bonding between organic coatings (e.g., epoxy primer and silicone alkyd) and an unabraded aluminum alloy (5052) specimen, which otherwise had poor adhesion. It was observed that the adhesion properties of epoxy primer were also dependent upon the functionality of the nanoparticles. Pretreatments containing nanoparticles (Nano II) with a higher concentration density of –OH adhesive functional groups exhibited higher adhesion to the primer than those containing nanoparticles (Nano I) with a lower [OH]/surface area at similar weight loading. Tape pull-off adhesion test (ASTM D-3379, Method A) rating of a commercial epoxy primer with a silicone alkyd top coat on pretreated 5052 panels with Nano I and Nano II were 4A and 5A respectively, while the rating was 1A in the absence of the pretreatment. This data was further supported by the salt fog test (ASTM B-117). Nanocomposite pretreated (Nano II) panels exhibited excellent corrosion protection behavior and strong bonding to the epoxy primer, even after being exposed in the salt fog chamber for 28 days. The overall corrosion protection performance of these panels was far superior to the samples with an unabraded surface, and comparable to those with a grit-blasted (SSPC-SP10) surface.

Opportunities

NEI Corporation recently created a wholly owned operating division called Corrosion Technology, to focus on this technology area. This division of NEI offers the opportunity to both end-users of coated lightweight metal parts as well as materials suppliers to partner and build relationships. Corrosion Technologies is also seeking investment to realize the full commercial benefit of the nanocomposite pretreatment technology.

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Cost-Effective Gadolinium-Containing Polymeric Material Deters Cosmic Radiation

The Pitch

The earth's magnetic fields deflect most charged particle cosmic radiation. But we are constantly exposed to a certain amount of this cosmic radiation, which when it interacts with the earth's atmosphere or other matter produces energetic neutrons. Since the early 1990s, neutron-induced upsets in sophisticated integrated circuits have been well-documented and are increasingly frequent. Cosmic radiation levels rise with increasing altitude and geomagnetic shielding is reduced at the poles. Therefore, high altitude polar flights increase the exposure of passengers to damaging cosmic radiation. A lightweight, cost-effective neutron shielding thermoplastic material to deter radiation that uses gadolinium as the neutron absorber has been developed by Hybrid Plastics, Inc.

The deleterious effect of cosmic radiation is its potential to ionize both biological and synthetic materials with which it interacts. For example, thermal neutrons (<0.25 eV) are of low enough energy to be captured by the ^{10}B isotope contained in the boro-phosphate-silicate glass used as a dielectric layer in complementary metal oxide semiconductor (CMOS) chips. Upon capture of a thermal neutron, the ^{10}B nucleus can undergo a fission process ($n + {}^{10}B = {}^{7}Li + \alpha + \gamma$). The ionizing products from the process include a 1.47 MeV α-particle and a 0.84 MeV Li nucleus. These in turn produce electron–hole pairs that damage the delicate electron–hole pair balance in semiconductors. Once the total electrical charge reaching a storage cell is larger than the critical charge sustaining the stored data, an upset in the logic occurs and a "soft error" takes place. A single fission event can produce a large number of electron–hole pairs over a distance as great as a micrometer in range. The consequence is that several layers of damaged memory logic can result.

The effect of cosmic radiation on biological tissue is less clearly defined but it is known that radiation exposure levels are influenced by a number of factors.

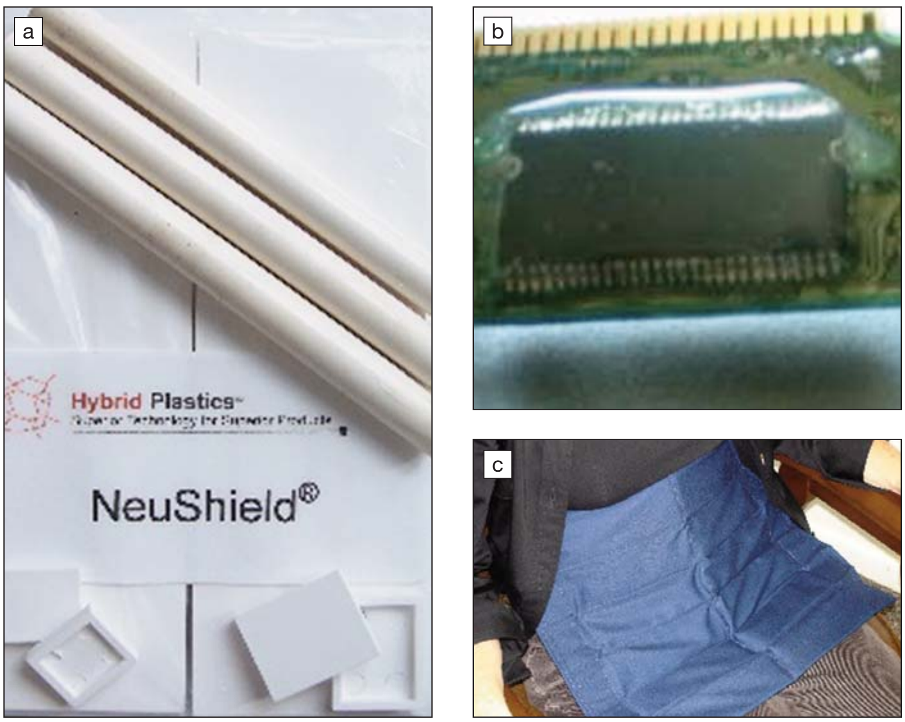

Figure 1. (a) NeuShield glue sticks, chip caps, and tape; (b) spot application to a radiation sensitive chip using a glue gun; and (c) lap apron for protection against cosmic radiation when in flight.

Most important are the Earth's magnetic field, atmosphere, altitude, and any shielding prospects from clothing, vehicles, and buildings. At an altitude of 35,000 feet, for example, the dose equivalent rate from cosmic rays is about 6 microsieverts (0.6 millirem) per hour, a significant fraction of which is directly due to neutrons. So a one-way transatlantic flight, in theory, is equivalent to having at least one chest x-ray.

The Technology

With respect to safety and affordability, gadolinium has been used for many years in thousands of patients, both adults and children, in the United States, Europe, and Japan, without any reports of serious adverse effects. The Food and Drug Administration (U.S. FDA) declared gadolinium safe for use in MRI and CAT scans in 1988. Gadolinium's cost of approximately \$130/kg makes it affordable for applications in healthcare, microelectronics, and metal alloys.

Hybrid Plastics produces a low-cost and readily deployable thermal neutron shielding material by melt blending gadolinium oxide and POSS® silanols with polyolefin polymers by using a twin screw extruder. Natural abundance Gd_2O_3 is the low-cost material of choice because it has a cross-section for thermal neutrons of 49,000 barns compared with isotopically enriched boron (3840 barns). On a bulk cost basis, Gd_2O_3 costs \$23.84/kg for 1000 kg compared with the lowest cost source of isotopically enriched boron, which is in the form of boron carbide particulates costing \$6500/5 kg (because of its limited supply).

The shielding material produced by Hybrid Plastics is marketed under the trade name NeuShield®. As formulated, a 2-mm thick layer of NeuShield (containing 60 wt% Gd_2O_3) eliminates 90% of thermal neutrons and 50 KeV x-rays. For electronic shielding, NeuShield is available in the form of hot-melt adhesive glue sticks for spot application (\$14.60/stick per 200 unit order), as premolded chip caps that easily fit over computer chips to reduce the effects of neutron-induced memory upsets (\$0.88/cap per 40,000 unit order), and as radiation-hardened duct tape strips (shown in Figure 1a,b). It is also available as a conveniently compact protective apron intended for in-flight use by pregnant flyers (shown in Figure 1c) and for transporting live tissue.

Opportunities

Hybrid Plastics is seeking strategic partners to adapt its NeuShield technology for applications in the medical field. In the electronics field, the company is interested in developing an industry standard for the radiation field and following up with cross-licensing agreements. Similar cross-licensing agreements are also being pursued for the aerospace and cosmetics markets.

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Holography Offers Cost-Effective Process for Fabricating Semiconductor Optical Components

The Pitch

An innovative technology for the holographic fabrication of semiconductor optical components with smooth relief-free surfaces has been developed by the Advanced Laser Technologies and Innovative Research Center (ALTAIR Center). The technology takes advantage of the effect of large refractive index change in the near surface region of various semiconductor materials, including GaAs, ZnSe, and CdS, under illumination with low intensity light. It uses direct optical recording of a refractive index structure instead of etching of a surface relief to control the light. The advantage of relief-free components becomes apparent when additional layers of crystal are to be grown or deposited onto a semiconductor surface. Crystalline growth is subject to stresses and flaws. However, it is more likely to yield near-perfect structures when starting from a smooth, perfectly flat substrate.

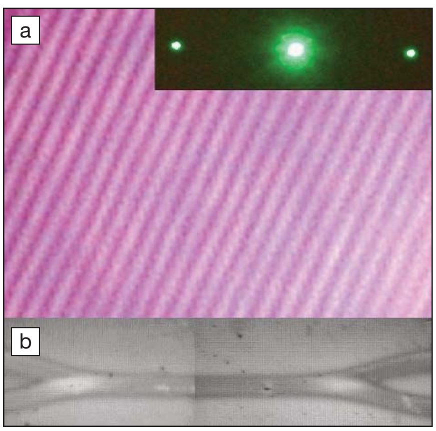

Figure 1. (a) Relief-free diffraction grating and (b) channel waveguide structure with high index contrast recorded on GaAs substrate. Inset shows diffraction of a probe laser beam reflected from the grating.

This new process is both efficient and cost-effective as it eliminates numerous steps involved in the commonly used photolithography technique: photoresist deposition, developing, and etching. It can be carried out at room temperature with minimal clean-room requirements and can even be applied to off-the-shelf products to improve their performance. The process is highly adaptable. It creates a productive technology platform for the fabrication of a broad range of products for a variety of markets, including infrared diffraction gratings for spectral devices, diffraction components for infrared optics, integrated optical components for signal processing, laser diodes with improved performance, and a new generation of photonic crystal semiconductor lasers.

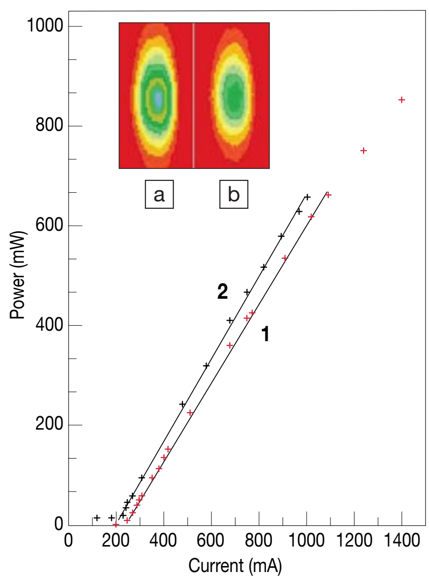

Figure 2. Power-current characteristics of a high-power laser diode before (1) and after (2) processing, demonstrating decreasing the laser threshold and increasing the slope efficiency. The inset shows a laser beam in the far field before (a) and after (b) processing, demonstrating decreasing the beam divergence.

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The Technology

Holographic diffraction gratings can be recorded in semiconductor materials using the interference of laser beams. Various waveguide structures can be recorded employing a system for projection photolithography with an appropriate photomask. Both a grating and a channel waveguide structure recorded on a GaAs substrate are shown in Figure 1. Although the surface of the substrate remains perfectly flat, the grating and the waveguide are clearly visible under an optical microscope due to the large contrast in the refractive index, approaching 0.8. The inset in Figure 1 shows the diffraction of a probe laser beam reflected from the recorded grating.

Recording the holographic gratings in GaAs and ZnSe, materials that are transparent at mid-IR wavelengths, enables the manufacture of relief-free, lightweight, thin-plate infrared diffraction optics, in which all required wavefront transformations can be performed at optical paths smaller than the light wavelength. The components of mid-IR optics include diffraction gratings, Fresnel lenses, beam splitters, polarizers, and retardation plates, employing the artificial birefringence of subwavelength periodic structures.

Optical recording in GaAs of high-aperture channel waveguide structures with high-index contrast operating at the key telecommunications wavelengths of 1.3 µm and 1.5 µm reduces losses associated with sharp bending and imperfect etching. This facilitates the high-density monolithic integration of various optoelectronic components. Holographic gratings recorded in such channel waveguides are useful for wavelength division multiplexing components. A prototype system for optical recording of channel waveguides with Bragg gratings operating as spectral filters or input and output beam coupling elements has been developed.

Local control of the properties of GaAs-based heterostructures suggests the potential for improving the performance of laser diodes by clearing defects from the laser gain region and adjusting the materials properties in the region of the output mirrors. Figure 2 shows decreasing the laser threshold current by 25–30% and increasing the slope efficiency after processing of a commercial off-the-shelf, high-power laser diode. The inset in Figure 2 shows a cross-section of the laser beam before and after processing, demonstrating a decrease in the beam divergence. The patented technology also allows adjusting the emission wavelength of an already fabricated laser diode by 15–20 nm. The holographic recording of periodic structures with high index contrast in close proximity to the gain region of a laser diode suggests the possibility of fabricating a new generation of high-power photonic crystal laser diodes exhibiting enhanced spectral brightness, plus improved thermal stability and beam quality.

Opportunities

ALTAIR Center, LLC is seeking strategic business partners for joint product manufacturing and licensing of the company's developed technology.

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