Canadian Company is Engineering Innovative Materials For the Future Of Metal Finishing

By James H. Lindsay, AESF Fellow

Attendees at AESF Week in January 2004 were treated to an outstanding keynote address very ably delivered by Dr. Francisco (Paco) Gonzalez, of Integran Technologies, Toronto, Ontario, Canada. In it, he outlined the future of nanotechnology and the impact that it has, and will have, on the metal finishing industry. That impact is considerable. Gonzalez is affiliated with Integran Technologies, Inc. Surrounded by a triangle of freeways within a stone's throw of Lester B. Pearson International Airport in Toronto, it is in the forefront of this rapidly emerging field.

Background

It is interesting to note that the origins of Integran, whose technology deals with things on a nanoscale, derived from an entity whose technology deals with things on a megascale. The company was a spin-off from Ontario Hydro, one of the larger power companies anywhere. Specifically, Integran was derived from Ontario Hydro Technologies, the research division, and founded in 1999. However, its previous incarnations have put it into the forefront of nanotechnology for at least 20 years.

After the then-Progressive-Conservative Party took the reins of power of the Ontario Government in 1995, one of their policies led to partial privatization and reorganization of Ontario Hydro, separating the power transmission function from power generation. In the aftermath, several members of the technical materials team at Ontario Hydro Technologies eventually formed Integran.

In addition to Gonzalez, now vice president of process and product development, the original core talents of this organization come from Dr. Gino Palumbo, president and chief executive officer, and Dr. Uwe Erb, scientific advisor, who also is professor in the Department of Materials Science and Engineering at the University of Toronto. Erb heads up the Nanomaterials Research Group at the University, and is one of the pioneers in the nanotechnology field. With this fortuitous connection, Integran draws on the talents and expertise of the faculty and students of this group.

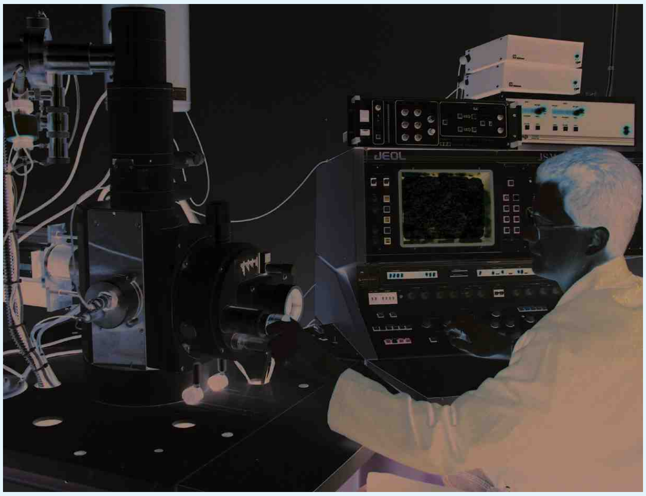
Integran serves its customers through material sales, contract manufacturing, technology licensing, material/process diagnostics, research and joint technology development. They have a world-class instrumental capability to produce and characterize the materials that they develop.

Nanomaterials are enhancing surface finishing technologies in many applications. Integran's Iain Brooks is shown here operating the plating cell for production of Nanoplate® materials.

The Basic Technology

Integran's specialty is in the area of intergranular materials, hence the name "Inte-gran." That is, they have developed proprietary material technologies that manipulate grain boundaries in materials to commercial advantage. Elegant in their simplicity, two basic concepts are the key to Integran's advanced technologies, one working from the "top down" and the other from the "bottom up."

The "top down" technology is called Grain Boundary Engineering (GBE).® It works from the top surface and acts "down" into the original material. The "bottom up" technology is called Nanoplate® and is used to build nanostructured layers "up" from the surface by electroplating. Both technologies wind up with nanostructured materials with mammoth improvements in a variety of properties. Both concepts go back to manipulation of grain boundaries.



Integran is a pioneer in developing and characterizing nanomaterials.

Why the interest in grain boundaries? Basically it is the disorder there. Crystalline materials have a regular array of atoms, which allow materials to be ***bent*** and/or ***stretched***, which is fine where ductility and formability are needed. In between the crystals are narrow (usually less than 1 nm) regions, which are disordered. These disordered regions frequently compromise the durability and longevity of structural components through processes like intergranular corrosion, cracking, creep, etc. Integran's top-down GBE process controls the degree of disorder in these regions. Using this top-down process, such important facets as fatigue and creep resistance as well as stress corrosion cracking resistance are enhanced far beyond what traditional metallurgical processing can accomplish.

On the other hand, Integran's bottom-up nanomaterial technology reduces the size of the perfect crystals to the range where they are nearly equivalent in diameter to the width of the disordered grain boundary regions between them. The smaller the grains, the larger the grain "surface" area, or the more grain boundary area. The smaller the grain size, the larger the amount of grain boundary material. Taken to the limit, perfect disorder would be in the amorphous state, where the grain size is that of a single atom.

The net result is an exponential enhancement of many physical properties, most of which have yet to be measured given the novelty of such nanocrystalline materials. Under conventional regimes, impurities in the alloys diffuse and migrate to the grain boundaries and precipitate there. In nanocrystalline systems, the impurities have so many boundaries to migrate to, that the end result is "homogenization by segregation." Hence there is reduced susceptibility to intergranular and stress corrosion cracking

Grain Boundary Engineering (GBE)

Integran's grain boundary engineering technology "beefs up," on a nanoscale, the structural order of grain boundaries in conventional metals and alloys. Erb describes this thermomechanical technology as a "beating and heating" operation. The operation can be applied to bulk materials, but more interestingly, it can also be applied as surface treatment to finished and semifinished components. The surface is first subject to shot peening (the "beating"). The surface layers are affected down to a depth of 100 to 1000 μm (4 to 40 mil). Does this sound like work hardening? Well, yes it does, but Integran's proprietary technology carries it all several steps further.

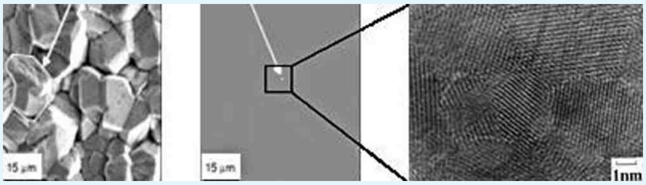
The "heating" portion of the process involves induction heating, which creates the "coating." This layer can be considered a coating in the sense that a chromate or phosphate conversion process produces a coating. The coating is made from the original surface layers of the substrate. And, they have found that as much as 60 to 70% of the volume in these layers is comprised of highly ordered grain boundary material. Once again, this all sounds deceptively simple, but Integran has spent many years to develop a proprietary technology that allows consistent, reproducible results.

The results show significant breakthroughs in enhancing critical engineering properties such as weldability, resistance to intergranular corrosion and stress corrosion cracking, sulfidation resistance, fatigue resistance and high temperature creep resistance. In Alloy 800, which is vulnerable to intergranular corrosion, tests have measured the reduction in corrosion rate from 2.2 to 0.22 mm/yr. In a nuclear waste container application using Hastelloy Alloy C22, testing via ASTM G-28 showed a reduction in corrosion rate from 4.3 to 2.5 mm/yr (170 to 100 mil/yr). The high temperature creep rate of Inconel Alloy 625 was reduced from 31.1% to 2.1% per year at 700°C (1292°F) under a load of 35 MPa (5000 lb/in^2).

Applications are too numerous to list, but a few are mentioned here. Increased stress corrosion cracking resistance is critical in nuclear steam generator tubing. Plates used in lead acid batteries, containing 0.06% Ca and 0.75% Sn in lead showed considerably increased life after GBE treatment resulting in longer lasting batteries. Alternatively, the electrode thickness can be reduced which results in a decrease in the total weight. It should be noted that the amount and nature of the alloying elements in the battery plates are very important. In addition, GBE has found application in jet engine components and several corrosion-resistant surface treatment applications.

Nanoplate®

Nanotechnology and the associated fabrication of nanomaterials are in the forefront of science and technology in the early years of the 21st century. The formation of nanostructural layers by electroplating is quite germane to the metal finishing industry, and this emerging technology promises to be a key element in the future of metal finishing.



Conventional nickel deposit (left) and nanocrystalline deposit (center and right).

Traditional electroplating offers the best and most effective means of producing these coatings, and wins out over more sophisticated deposition techniques. This isn't the first time this has happened. Using proprietary pulse plating protocols and electrolyte chemistry, grain sizes as small as 10 nm are routinely deposited. The figure above shows the surface morphology of a conventional nickel electrodeposit at the left. In the center is a similar photo, at the same scale, of a nanocrystalline deposit. At right is an enlargement of the center photo showing the dramatic difference in size of the nanoscale grains.

While the other methods, including vapor deposition and chemical synthesis can yield similar grain sizes, Integran's plated nanolayers are applicable to more sizes and shapes of work pieces, including strip, plate, wire and rod. With the non-line-of-sight aspect of electrodeposition, complex-shaped articles, including microcomponents, can be plated. And inherently thick industrial coatings can be produced by plating. It should be stressed that Integran's electrodeposited nanomaterial technology produces

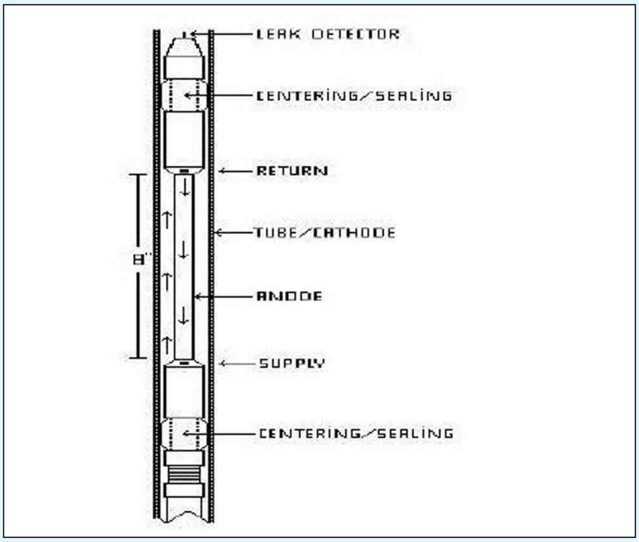


Fig. 2—Electrosleeve probe for in-situ structural repair of degraded steam generator tubing.

deposits that are solid and fully dense materials and not powdery.

Costs are lower than other competing technologies, as is true with so many more traditional plating applications. Both batch and continuous processing are possible, and net shape or near net shape products can be formed (*i.e*., electroformed nanomaterials).

The basic research for the Nanoplate® technology was worked out in the 1980s, from Dr. Erb's work then at Queen's University in Ontario, and presently at the University of Toronto. The resulting deposits are fully dense, and many different metals, alloys and metal matrix composites have been produced by this approach.

The first application of these electrodeposited nanocrystalline materials was based on this research, in the nuclear power industry, in collaboration with Dr. Gonzalez and other scientists and engineers at Ontario Hydro, in 1994. The resulting Electrosleeve® (see figure above) technology has been used in the repair of steam generator tubing in nuclear power plants in the US and Canada.

In this application the electrodeposited nanostructured material was >99.5% nickel containing microalloyed phosphorus. The deposit was, for all practical purposes, free of macroscopic defects and porosity and had an average grain size of approximately 50nm. The mechanical properties, compared with conventional electrodeposited nickel, are shown in the table below. Note that the increase in strength is realized at relatively high ductility, with no change in Young's modulus. To date, nanomaterials made by other techniques do not possess the twin attributes of high strength and ductility. The lack of voids in the full-density Nanoplate® materials is the reason.

This Nanoplate® technique can be used for structural repairs of tubes and pipes in both inside and outside diameters in both CANDU (in Canada) and pressurized water reactors (in the U.S.). Far beyond this, a multitude of applications has successfully used this technology. Materials have been coated with nanocrystalline deposits by barrel, rack and even selective brush plating. In addition to coatings, free standing electroforms have been fabricated, from foils to net-shape articles.

The search for chromium replacement coatings has been a critical issue for many years. Nanocrystalline materials have found success in providing solutions to this need. For example, nanocrystalline cobalt-phosphorus coatings have been found to provide superior lubricity and sliding wear resistance when compared to hard chromium. Corrosion protection is also reported to be better.

Another metal replacement need is in the area of cadmium substitutes. Here, nanocrystalline zinc-based coatings can meet the property requirements that cadmium would supply: low contact resistance, lubricity, ductility and sacrificial corrosion resistance.

Other interesting successes include a nanocrystalline nickel containing molybdenum disulfide for lubricity purposes. The same nickel matrix, containing particulate samarium-cobalt provides enhanced hard magnetic properties. Indeed, the nanostructured soft magnetic materials provide the proper magnetic properties with strong mechanical properties, a combination not readily available with conventional materials, including grain-oriented silicon steel and melt-spun amorphous alloys. Nanocrystalline iron-cobalt-nickel alloys can be electroformed as sheets as low as 100 μm (4 mil) in thickness, and foils down to 10 μm (400 μ-in.). Integran has developed a soft magnetic Nanoplate® coating with a composition similar to that of Permalloy that is being used industrially in high sensitivity flow meters.

Of course, the story is nowhere near completion. The emergence of MEMS (micro electromechanical systems) has spawned the fabrication of nickel-molybdenum and other alloy micro-components such as springs, levers, diaphragms, etc. This is a taste of things to come for our industry, and Integran is well-positioned to be an important player.

The point is that nanomaterials may at first glance sound obscure to some, but nothing could be further from reality. As you can see, a variety of down-to-earth applications, from chromium replacements to anti-corrosion protective coatings, already benefit from the use of nanomaterial coatings, and they are produced on racks, in barrels, and even by brush plating on strip, sheet, wire and rods, among other shapes. The quantum leap in properties that is attainable portends good things for the future of the metal finishing industry. Integran is looking forward to working with customers to apply its materials to the demanding challenges of future technologies. Nanoplate® products, because of their small grain size and superb specific strength, may be the required solution for many material problems now facing MEMS and other nanotechnology applications. Integran can support the development work needed by customers with its highly qualified personnel in its well equipped electroplating and metallurgical laboratories to meet these challenges.

Property	Conventional Ni*	Electrosleeve
Yield Strength, 25°C (77°F)	103 MPa (14.9 Kpsi)	667 MPa (96.7 Kpsi)
Yield Strength, 350°F (662°F)	---	492 MPa (71.3 Kpsi)
Ultimate Tensile Strength, 25°C (77°F)	403 MPa (58.5 Kpsi)	855 MPa (124.0 Kpsi)
Ultimate Tensile Strength, 350°F (662°F)	---	714 MPa (103.5 Kpsi)
Elongation, 25°C (77°F)	50%	15-23%
Modulus of Elasticity, 25°C (77°F)	207 GPa (30.0 Mpsi)	204 GPa (29.6 Mpsi)
Modulus of Elasticity, 350°C (662°F)	---	179 GPa (26.0 Mpsi)

*ASM Handbook, Vol. 2, ASM International, Materials Park, OH, 1993.