# Electroplated Nanostructures for Functional and Structural Applications

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## Abstract

Nanotechnology is an exciting and rapidly evolving new field that deals with the design of extremely small structures having critical length dimensions on the order of only a few nanometers. One particular subfield of nanotechnology deals with nanostructured materials in which this critical dimension is the crystal size.

This paper focuses on nanostructured materials produced by electrodeposition methods which, over the past decade, have already been advanced from the research laboratory to an economically viable nanomaterials technology. The overall objectives of this paper are to provide answers to the questions, "*what nanotechnology means in the context of metalfinishing?*" and "*what opportunities exist for electroplating industries?*"

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## Introduction

In a recent article entitled "Review & Forecast: A Cosmopolitan Perspective" in the January, 2004 issue of *Metal Finishing*, A. Kuhn presented an excellent summary on the state-of-the-art of the metal-finishing industry in the broad context of recent world political events and global socio-economic developments [1]. In this article, reference was made to a series of highly-organized, nanoporous metal and metal oxide films prepared by electrodeposition in a liquid crystal template, a technology introduced in 2003 by Nanotexture, a British company developing applications for these materials in the areas of supercapacitors, gas sensors, fuel cell electrodes and filtration membranes for biological materials. With respect to Nanotechnology, the author then posed the following question, "*Could it be that 2004 might be the year when we discover what nanotechnology really means in the context of metal finishing?*"

The authors of the present article believe that, to a large extent, we have already been going through this discovery phase for more than a decade. Nanostructured electrodeposits have been developed for a number of applications including wear and corrosion resistant coatings (e.g., Cr replacement coatings), soft magnetic materials, microelectromechanical systems (MEMS, see article by Cheung *et al.*, in this session), in-situ repair for degraded nuclear steam generator tubing, etc.. The latter technology was likely the first large scale industrial application of structural nanocrystalline materials in the world, which was developed in the early 1990s and has been implemented since 1994 as the so-called Electrosleeve Technology in several Canadian and U.S. nuclear reactors. The central component of this technology is a nanostructured Ni-microalloy coating, electrodeposited up to a thickness of about 1mm on the inside of nuclear steam generator tubing, and using quite conventional electroplating technology, modified to the specific needs for this particular applications [2,3].

In this paper, we first present a brief overview of current developments in the area of nanotechnology. This will be followed by a short review of the history of nanomaterials with particular emphasis on the development of electroplated nanostructures. The synthesis and important structure-property relationships of nano-electroplated materials will be discussed and a comparison of various synthesis techniques for nanocrystal production will be presented. Finally, several examples of current applications of various electroplated nanomaterials will be given.

## Nanotechnology: The Next Industrial Revolution

It is now generally accepted that "**nano**", the latest buzzword in science and technology, will form the basis for the next industrial revolution. Controlling and manipulating matter on the length scale of one nanometer (one billionth of a meter), which is the size domain of atoms and molecules, has been the dream of scientists for many years. Today, it is nearly impossible not to find "nano" attached, in one way or another, to almost everything we do in science and technology. Some examples of the many different facets of nanotechnology are summarized in Figure 1. This field is growing so rapidly that even the expert in one particular subfield has difficulties in keeping up with all the latest developments in this technology.

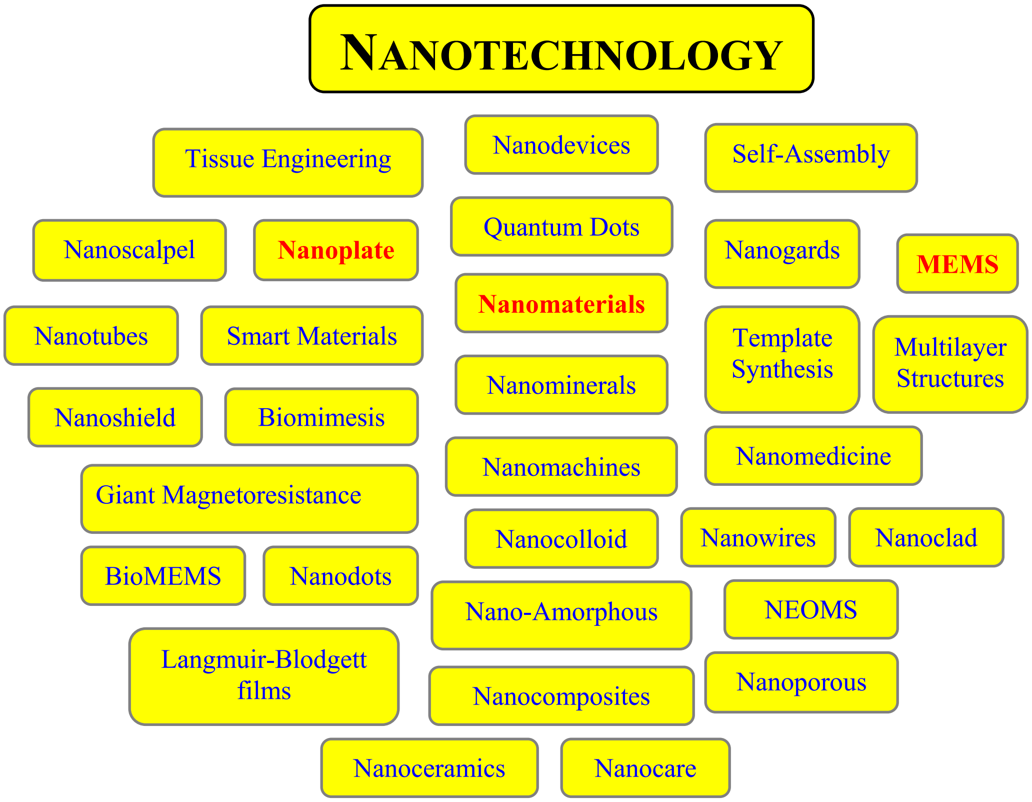


*Figure 1 Examples of the many aspects of nanotechnology in random order.*

Nanotechnology is an interdisciplinary field involving people with very different backgrounds: physicists, chemists, biologist, medical professionals, electrical engineers, mechanical engineers, chemical engineers, materials scientist… and, of course, electroplaters.

The key areas in today's nanotechnology arena are shown in Figure 2. They include biology, medicine electronics, materials, devices and tools. This technology has not only captured the attention of researchers and business people, but also enjoys enormous public interest, in particular following the announcements in recent years of strategic government-sponsored nanotechnology initiatives in many countries around the world. For example, in the United States, following President Clinton's initial 1999/2000 Nanotechnology Initiative, the *21st Century Nanotechnology Research and Development Act* was signed by President Bush on December 3, 2003, which will provide $3.7 billion of funding over the next four years (see Figure 3 for details).

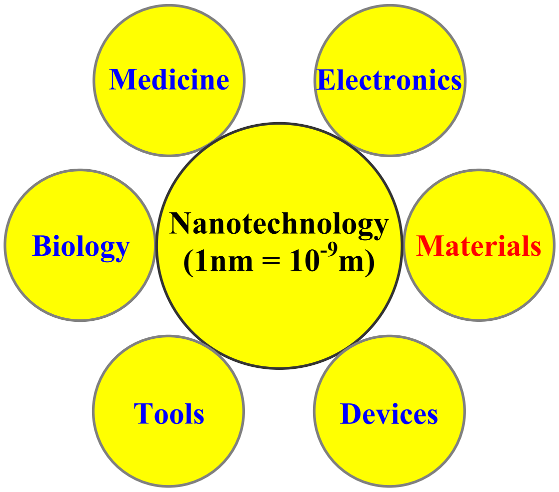


*Figure 2 Main focus areas of nanotechnology.*

**Nanotech R&D act becomes law**

By R. Colin Johnson
EE Times
December 03, 2003 (11:54 AM EST)

PORTLAND, Ore. – President Bush signed into law the 21st Century Nanotechnology Research and Development Act on Wed. (Dec.3), which has been approved by both Houses of Congress after months of haggling.

The $ 3.7 billion appropriation will be divided among eight government agencies: National Science Foundation, Department of Energy, National Aeronautics and Space Administration, National Institute of Standards and Technology, the Environmental Protection Agency, Department of Justice, Department of Transportation and the Department of Agriculture (NSF, DOE, NASA, NIST, EPA, DOJ, DOT, DOA, respectively).

According to California House Representative Mike Honda, nanotechnology "the worldwide market for nanotechnology products and services could reach $ 1 trillion by 2015".

*Figure 3 Announcement of U.S. 21st Century Nanotechnology Research and Development Act [4].*

Nanotechnology is predicted, by the U.S. National Nanotechnology Initiative to have an enormous potential impact over the next 20 years. The projected market size is more than $1 trillion US/year by 2015 in eight main sectors:

| | | | |
|---|---|---|---|
| • Materials | $340 billion | • Aerospace | $70 billion |
| • Electronics | $300 billion | • Sustainability | $45 billion |
| • Pharmaceuticals | $180 billion | • Healthcare | $30 billion |
| • Chemicals | $100 billion | • Nanotech Tools | $20 billion |

In a recent press release, Business Communications Company, Inc. has presented figures regarding the short term projections as analyzed in a major market evaluation [5]. In their analysis, the total global demand for nanotechnology products (materials, tools and devices) for 2003 was estimated at $7.6 billion. For the next few years, they expect an average annual growth of over

30%, with the market reaching close to $30 billion by 2008 (Figure 4). They further concluded that the market will grow more than twice as fast as either the biotechnology sector or the informatics market.

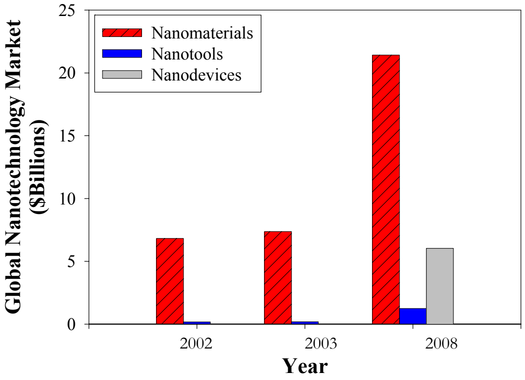


*Figure 4 Global Nanotechnology Market, 2002, 2003 and 2008 [adopted from reference 5].*

Regarding the overall efforts as measured, for example, by R&D expenditure, number of start-up companies, patents issued, etc., the United States is currently considered the leader in this technology, followed by Germany in Europe and Japan in East Asia [6].

In order to meet industry's future demands in terms of highly trained personnel, many Universities around the world have introduced "nano-options' in their undergraduate programs which cover various aspects of this technology. For example, at the University of Toronto, Nanotechnology is an option in the Engineering Science Program in which students are exposed to a broad range of nanotechnology topics. The first group of students in this program graduated in 2003, and all of them entered graduate programs at various top ranking schools in the United States, Canada and Europe.

## History of Nanostructured Materials

The area of nanostructured materials is the most advanced subfield of nanotechnology which has its origin in the early 1980s [7]. Over the past 20 years, close to 200 different methods have been introduced to produce nanostructured materials in many different shapes and product forms. On the basis of the underlying fundamental physical and chemical principles, the different processing routes can be classified into five distinct groups as shown in Table 1.

*Table 1 Different Approaches for Nanocrystal Synthesis.*

| Processing Route | Specific Examples |
|---|---|
| Vapour Phase Processing | Physical Vapour Deposition<br>Chemical Vapour Deposition<br>Inert Gas Condensation |
| Liquid Phase Processing | Rapid Solidification<br>Atomization<br>Sonication of Immiscible Liquids |
| Solid State Processing | Annealing of Amorphous Precursors<br>Mechanical Attrition<br>Equal Channel Angular Processing |
| Chemical Synthesis | Sol-gel Processing<br>Precipitation<br>Inverse Micelle Technology |
| Electrochemical Synthesis | Electrodeposition<br>Electrodeposition Under Oxidizing Conditions<br>Electroless Plating |

Many nanomaterials are no longer scientific curiosities but have already moved from the research laboratory to full scale production. Examples of nanostructured materials products currently available are listed below, including two groups of electroplated materials:

| Product Name | Company | Product Description |
|---|---|---|
| Nanocare | Nano-Tex (U.S.A.) | Stain-resistant fabrics |
| Nanoceram | Argonide Nanomaterials (U.S.A.) | Alumina nanofibres |
| Nanoclay | Southern Clay Products (U.S.A.) | Nanocrystalline clay additives |
| Nanograin | Nanodyne Corp. (U.S.A.) | Ceramic, metal and composite powders |
| NanoPhaze | Nanophase Materials Corp. (U.S.A.) | Metals and ceramic powders |
| NanoPlate | Integran Technologies (Canada) | Electrodeposited metals, alloys and composites |
| NanoSurface | Advanced Surface Engineering (U.S.A.) | Nanocrystalline ceramic coatings |
| NanoTek | Nanophase Technologies (U.S.A.) | Nanocrystalline metals and oxide powders |
| Nucryst | Nucryst Pharmaceuticals (Canada) | Antimicrobial silver nanocrystals |
| Vitroperm | Vacuumschmelze (Germany) | Nanocrystalline soft magnets |
| Amplate | Fidelity Corporation (U.S.A.) | Amorphous / nanocrystalline electrodeposits |
| Finemet | Hitachi Metals (Japan) | Nanocrystalline soft magnets |

Some of the highlights of our own activities in the area of nanocrystalline electrodeposits that are of importance to the community served by AESF are as follows:

- 1983 – Initiated major research effort on nanocrystal synthesis by electrodeposition (U. Erb *et al.*, Queen's University, Canada)
- 1989 – First paper on nanocrystalline Ni-P electrodeposits [8]
- 1992 – Initiated Electrosleeve Technology [2, 3]
- 1994 – First patents on nanocrystal synthesis [9,10]
- 1995 – First report on nanocrystals at AESF SUR/FIN [11]
- 2001 – Presented several papers at AESF SUR/FIN Nashville [12-15]
- 2002 – Presented several papers at AESF SUR/FIN Chicago [16-18]
- 2002 – Participated in establishment of AESF Nanostructured Materials Subcommittee

- 2003 – Presented paper on “Nanotechnology Opportunities for Electroplating Industries” in *Plating and Surface Finishing* [19]
- 2003 – Presented paper at AESF / EPA meeting [20]
- 2003 – Co-organized full day session and presented several papers at AESF SUR/FIN Milwaukee [21-24]
- 2004 – Co-organized full day session at AESF SUR/FIN Chicago

## Structure and Properties of Nanocrystalline Electrodeposits

Nanostructured materials can be produced in many different forms including clusters, cluster assemblies, colloids, powders, wires, rods, thin films, thick films, and bulk structures. Although electrodeposition is amenable to produce many of these product forms, the following discussion will be limited to porosity-free (i.e., fully dense) materials as this is the form most frequently encountered in the electroplating industry. The distinguishing feature of a fully dense nanocrystalline metal is its large volume fraction of atoms associated with the intercrystalline network consisting of grain boundaries and triple junctions which separate nano-sized grains in different crystallographic orientations. This volume fraction can be computed by using reasonable assumptions for grain shape and thickness of typical grain boundaries [25].

Using a regular 14 sided tetrakaidecahedron as a grain shape (a reasonable assumption for an electrodeposit with equiaxed grain shape, Figure 5a) and a grain boundary width of about 1nm, the volume fraction of the interface component (i.e., atoms located at grain boundaries and triple junctions) is found to increase rapidly from a value much smaller then 1% for crystal sizes larger than 1µm (i.e., for conventional polycrystalline metals) to more than 50% for grain sizes less than 6 nm (Figure 5b). Figures 5c and 5d show brightfield and high resolution electron micrographs of a nanocrystalline nickel electrodeposit, respectively.

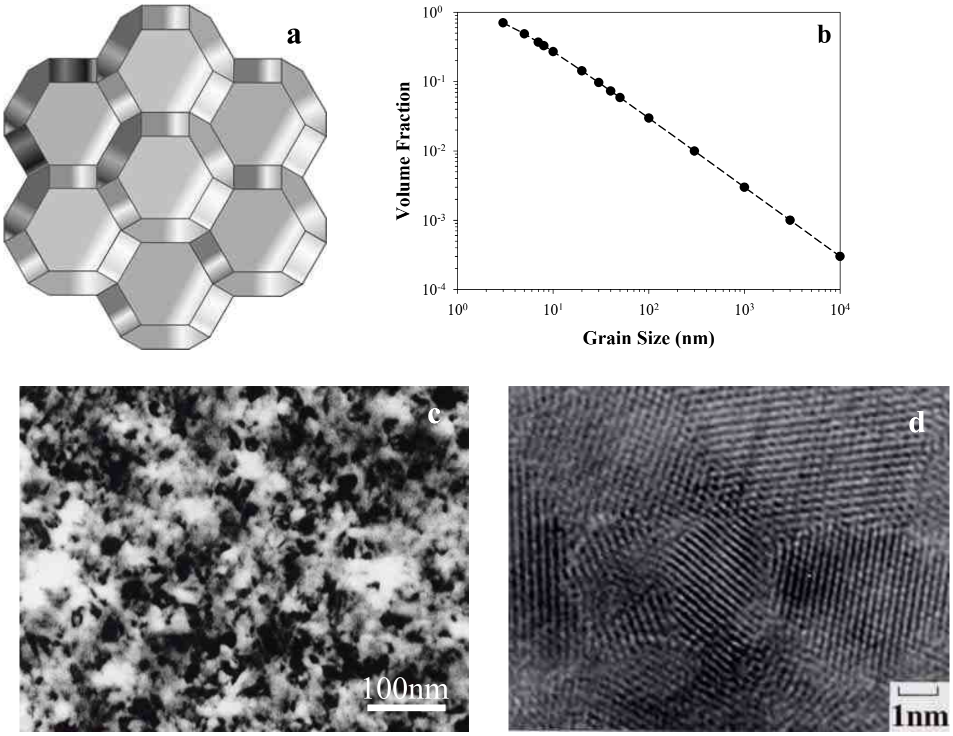


*Figure 5 (a) Grain shape assumption, (b) intercrystalline volume fraction, (c) an actual brightfield and (d) high resolution electron micrographs of nanocrystalline nickel.*

A direct consequence of the large volume fraction of interfacial atoms in nanocrystalline electrodeposits is that many of their physical, chemical and mechanical properties are enhanced compared with conventional polycrystalline and amorphous materials.

The effects of grain size on many properties have been extensively studied for electroplated nanomaterials, in particular Ni electrodeposits [26]. For example, Figure 6 shows that the hardness and yield strength of nickel electrodeposits are enhanced significantly by reducing the crystal size from 10µm to 10nm. On the other hand, the Taber wear index [13] (a measure of wear resistance, with lower numbers indicating lower wear rates) and coefficient of friction [26] of nanocrystalline nickel are much lower than for polycrystalline nickel; all of these being important improvements for wear applications.

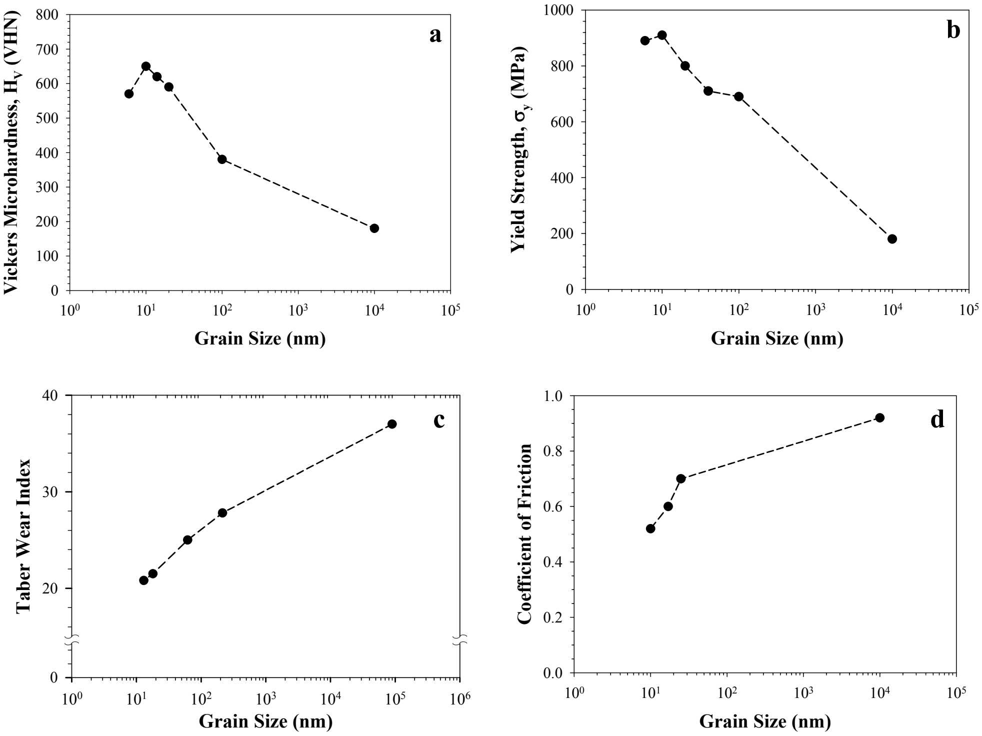


*Figure 6 Effect of grain size on various properties of electrodeposited nickel.*

The difference in the wear surfaces after a Taber wear test (using a CS-17 abrasive wheel) is quite impressive as shown in Figure 7 for polycrystalline and nanocrystalline nickel.

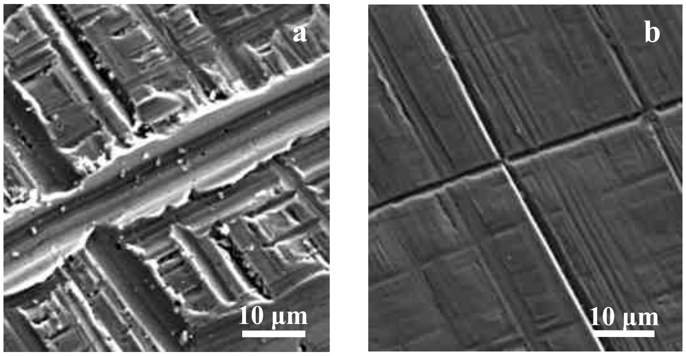


*Figure 7 Comparison of worn surfaces of (a) polycrystalline and (b) nanocrystalline nickel after Taber wear testing* [13].

Contrary to earlier expectations, the corrosion behavior of nanocrystalline nickel is not compromised by the high density of intercrystalline defects (grain boundaries and triple junctions) [15,18,23]. Despite a somewhat higher overall dissolution rate in some environments, nanocrystalline nickel shows great resistance to localized grain boundary attack (Figure 8).

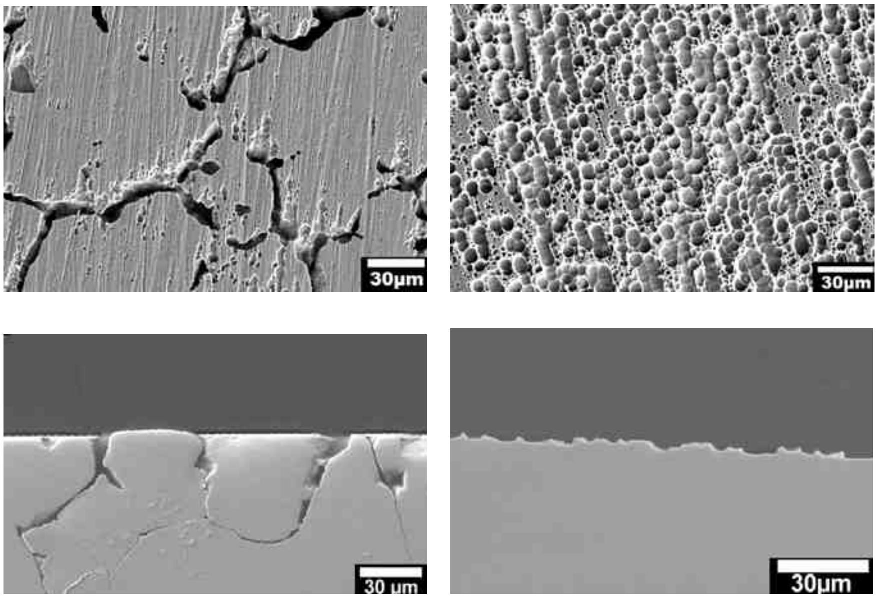


*Figure 8 Top view (top) and cross-sectional view (bottom) scanning electron micrographs of conventional polycrystalline Ni (left) and nanocrystalline Ni electrodeposits (right) after potentiodynamic polarization in 0.25M $NaSO_4$ solution* [19].

The delocalized corrosion observed for nanocrystalline nickel is of significant technological importance for applications in which localized corrosion of conventional nickel can result in catastrophic failure. The relatively uniform corrosion with predictable corrosion rates of nano-Ni is also of importance in lifetime assessment considerations of components for specific industrial applications.

## Nanocomposite Electrodeposits

As with conventional materials, certain properties can be further enhanced by incorporating second phase particles into nanocrystalline electrodeposits. The improvement of mechanical properties has been demonstrated using two different approaches. In the first approach, nanocomposites were prepared by a co-deposition process, very similar to the preparation of conventional co-deposits (i.e., by addition of SiC particles to a Ni plating bath) [27]. Figure 9 shows how the mechanical properties of nanocrystalline Ni with 1.8% SiC (400nm particle size) can be improved in comparison to conventional Ni-7% SiC electrodeposits.

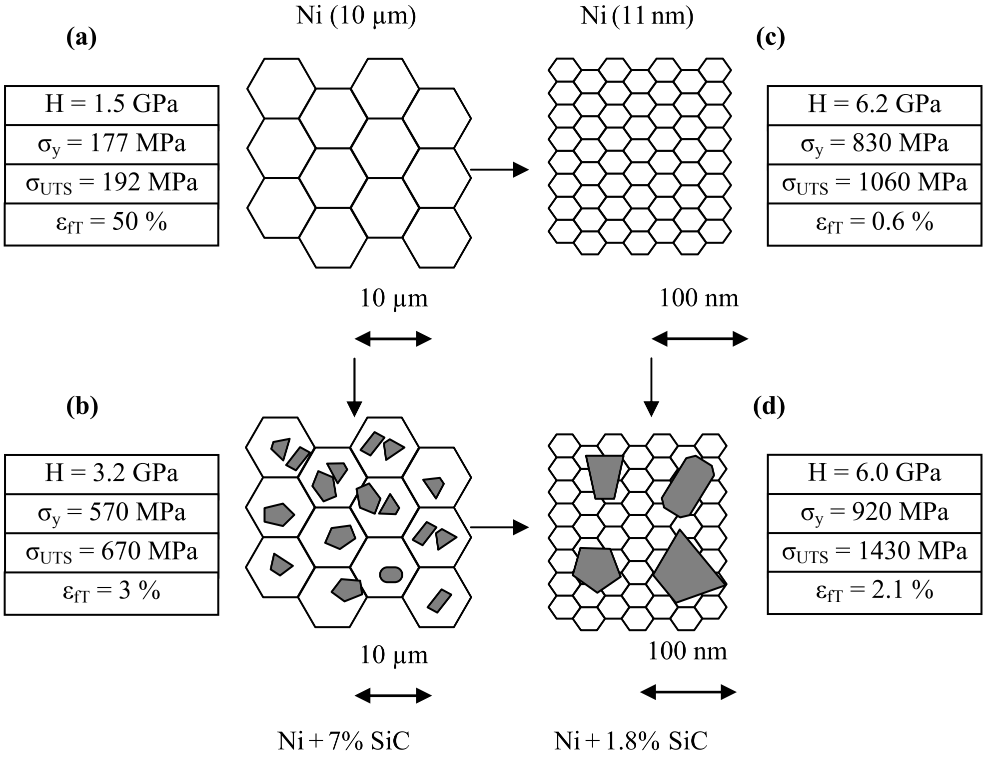


*Figure 9 Hardness (H), yield strength ($\sigma_y$), tensile strength ($\sigma_{UTS}$) and ductility in tension ($\varepsilon_{fT}$) for polycrystalline (a) and nanocrystalline (c) pure nickel as well as polycrystalline (b) and nanocrystalline (d) nickel-silicon carbide composite electrodeposits* [28].

In the second approach, the composites are produced by an in-situ annealing treatment of supersaturated solid solution deposits. For example, as-plated single phase Ni-P electrodeposits transform upon heat treating to a two-phase nanocomposite structure containing finely dispersed nanoparticles of $Ni_3P$ in a nanocrystalline Ni matrix [29]. In other words, Ni-P electrodeposits are age-hardenable as shown by the annealing curves in Figure 10, which demonstrate considerable hardness increases after short (15 – 20 minutes) annealing times at 400°C. Longer annealing times or higher annealing temperatures show the classical overaging effect, characterized by excessive grain growth of the nickel matrix and rapid $Ni_3P$ particle coarsening. The wear property enhancements that can be achieved through an appropriate heat treatment are summarized in Figure 11.

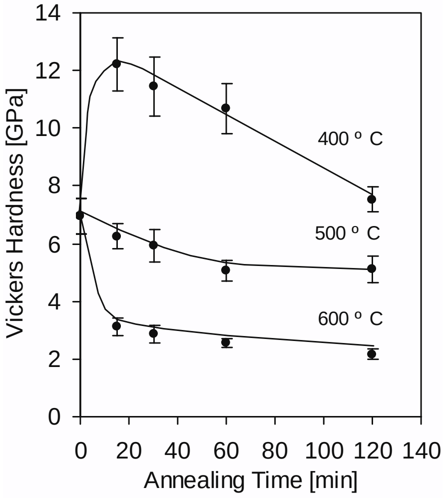


*Figure 10 Vickers hardness vs. annealing time for heat treatable Ni-P nanocrystals* [29].

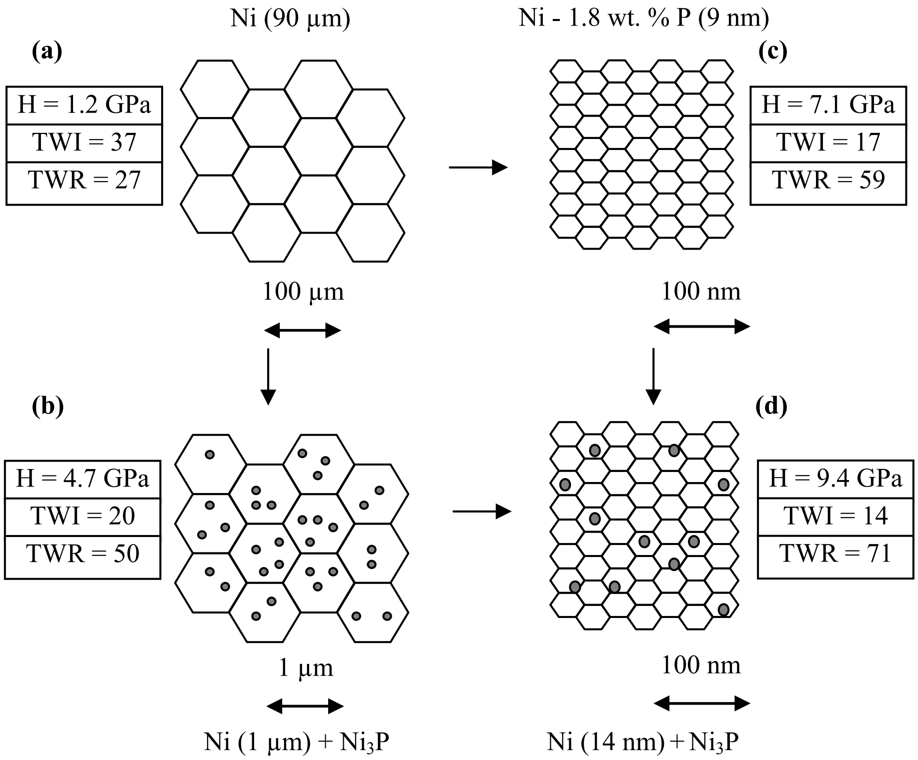


*Figure 11 Comparison of abrasive wear property improvements in conventional (a,b) and nanocrystalline (c,d) Ni-P alloys through heat treatment (TWI: Taber wear index; TWR: Taber wear resistance; H: hardness)* [28].

## Synthesis of Nanocrystalline Electrodeposits

The electrodeposition of metals from aqueous solutions involves several steps including mass transport of ionic species from the bulk electrolyte through the Nernst double layer, adsorption and desorption of adions on the cathode, surface diffusion of adions on the substrate surface, nucleation of new crystals and growth of existing crystals. Some of these steps are summarized in the simplified schematic diagram shown in Figure 12. The two most important steps in the context of nanostructure formation are nucleation of new crystals and growth of existing nuclei. It is well established that the competition between nucleation and growth is strongly influenced by parameters such as bath composition, pH and temperature as well as physical parameters such as stirring rate of the solution or current density. All of these are parameters which can be easily controlled in virtually all electroplating shops.

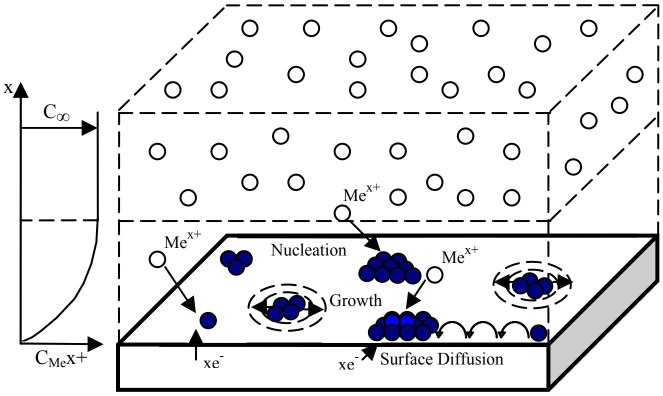


*Figure 12 Schematic diagram showing various steps during electrodeposition.*

In many electroplating operations, the conditions are such that very fine grains are produced in the early stages of deposit growth. However, with increasing deposit thickness a transition is observed from equiaxed fine grains to coarse columnar grains which is mainly the result of the growth competition between grains in different crystallographic orientations. The result is an electrodeposit which, in cross-section, shows considerable gradients in grain shape and size, with most of the final grain sizes being larger than 1µm. In contrast, if the electroplating parameters are chosen such that massive crystal nucleation dominates over crystal growth competition at any given stage in the plating process, a nanocrystalline structure throughout the entire thickness can be obtained. The structural difference between conventional and nanocrystalline deposits is shown in Figure 13. The electroplating conditions leading to nanostructure formation have been described elsewhere and basically include the application of pulsed current plating technology and/or the use of appropriate grain refiners [9,10]. Using this approach we have produced a large number of electrodeposits (Table 2) including pure metals, alloys and composite materials.

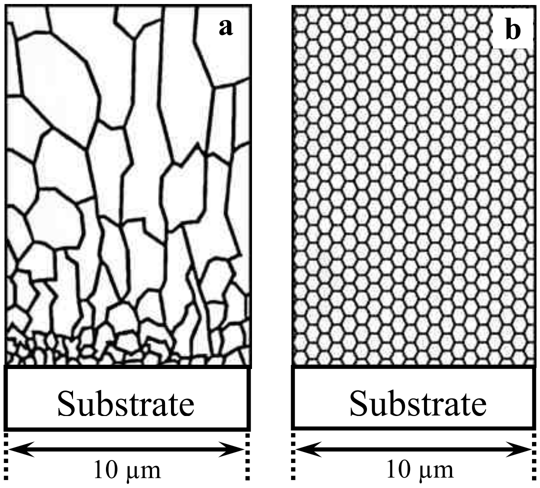


*Figure 13 Cross-sectional structure of (a) conventional and (b) nanocrystalline electrodeposits.*

*Table 2 Examples of metal alloys and composites produced by Integran's Nanoplate.*

| | |
|---|---|
| Pure Metals | Nickel, Cobalt, Copper, Palladium, Gold, Tin, Lead, Zinc |
| Alloys | Nickel-Phosphorus, Cobalt-Phosphorus, Nickel-Iron, Cobalt-Tungsten, Zinc-Nickel, Nickel-Cobalt, Nickel-Molybdenum |
| Composites | Nickel-Silicon Carbide, Nickel-Boron Carbide, Nickel-Nickel Phosphide, Cobalt-Silicon Carbide, Cobalt-Aluminum Oxide, Cobalt-Teflon |

## Comparison of Nanomaterials Production Methods

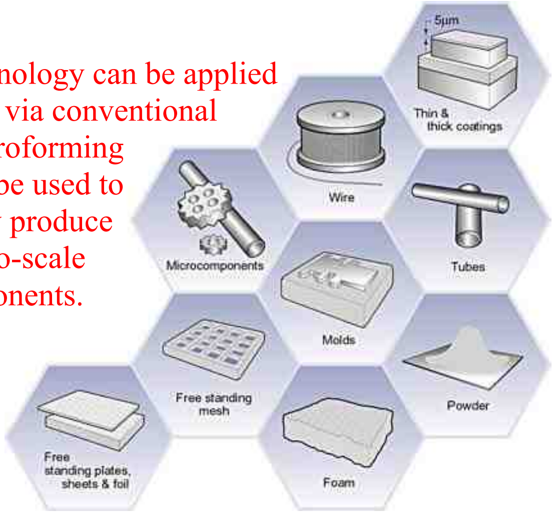
As pointed out in Table 1, there are many different methods of producing nanocrystalline materials. Comparing representative techniques of each of the five main approaches, it is quite obvious (Table 3) that electroplating has numerous advantages over many of the other approaches in terms of materials that can be produced, product forms, process type and product integrity. It is important to point out that the production of nanomaterials by electrodeposition methods is a very cost-effective technology. Unlike some of the other methods, it does not require major capital investment. Existing plating facilities can be used with only minor modifications with respect to power supplies and bath chemistries. As such, the technological and economical barriers to enter the nanomaterials market are much smaller as compared to some of the other production techniques.

*Table 3: Comparison of Nanomaterial Production Methods.*

| Achievable Grain Size | Electrodeposition <10nm | Inert Gas Condensation <10nm | Chemical Synthesis <10nm | Equal Channel Angular Pressing >50nm | Mechanical Attrition/Milling <10nm |
|---|---|---|---|---|---|
| ***Materials*** | | | | | |
| Metals & Alloys | ✓ | ✓ | ✓ | ✓ | ✓ |
| Ceramic Powders | ✓ | ✓ | ✓ | | ✓ |
| Composites | ✓ | ✓ | ✓ | ✓ | ✓ |
| Polymers | | | ✓ | ✓ | |
| ***Product Forms*** | | | | | |
| Powder | ✓ | ✓ | ✓ | | ✓ |
| Industrial Coatings | ✓ | | | | |
| Thin Coatings | ✓ | | ✓ | | |
| Thick Coatings | ✓ | | | | |
| Non Line of Sight Coatings | ✓ | | | | |
| Microfoils (unsupported) | ✓ | | | | |
| Sheet/Strip | ✓ | | | | |
| Plate | ✓ | | | ✓ | |
| Wire | ✓ | | | ✓ | |
| Rod | ✓ | | | ✓ | |
| Microcomponents | ✓ | | ✓ | | |
| Complex Shapes | ✓ | | | | |
| Multilayers | ✓ | | ✓ | | |
| Foams | ✓ | | | | |
| ***Process Type*** | | | | | |
| Low Cost | ✓ | | ✓ | | ✓ |
| Continuous | ✓ | | | | |
| Batch | ✓ | ✓ | ✓ | ✓ | ✓ |
| Net Shape | ✓ | | | ✓ | |
| Single Step Component Processing | ✓ | | | ✓ | |
| ***Product Integrity*** | | | | | |
| Porosity-Free | ✓ | | | ✓ | |
| Contaminant-Free | ✓ | ✓ | ✓ | ✓ | |

## Applications

Over the past several years, we have reported extensively on current and future applications of electrodeposited nanocrystals, at several AESF events [11-24] and elsewhere. In many applications, thin coatings are electroplated onto various substrates to modify specific surface properties (e.g., corrosion resistance, wear resistance, lubricity, magnetic properties) for various structural or functional applications. However, it should be pointed out that there are several other electrodeposition processes (e.g., brush-plating, electrowinning and electroforming) that can be used to produce nanocrystalline materials in many other shapes and forms including very thick overlay coatings, free-standing foils, sheets, plates, foams, wires and tubes as well as complex shapes and even powders (see Figure 14).



Nanoplate technology can be applied as a coating or, via conventional net-shape electroforming processes, can be used to cost-effectively produce micro- or macro-scale complex components.

*Figure 14 Various product forms that can be produced with nanocrystalline structures by electrodeposition.*

Table 4 summarizes some of the applications that we have previously presented at AESF events. These applications cover a wide range of products of interest to different customers including aerospace, automotive, power generation, microelectronics, consumer product and defense industries.

*Table 4 Applications of electrodeposited nanocrystalline previously discussed.*

| **Applications** | **Materials** | **References** |
|---|---|---|
| Battery grids | Pb | 19 |
| Catalysts for hydrogen evolution reaction | Ni, Ni-Mo | 11 |
| Chromium Cr-replacement coatings | Co, Co-P, Co-Fe, Co-Fe-P | 14,19,20 |
| Corrosion resistant coatings | Ni, Zn-Ni, Co, Co-P, Co-Ni,-Fe, Ni-SiC | 11,12,15,18,19, 21,23 |
| Electronic Connectors | Ni | 11 |
| Foil for printed circuit boards | Cu | 19 |
| Free standing soft magnet foil | Ni, Co, Co-Ni-Fe | 21 |
| Hard facing applications | Ni, Ni-SiC, Ni-$Al_2O_3$, Co, Co-P, Co-Fe-P | 16 |
| Heat exchanger repair | Ni-P | 11,12,19,24 |
| Magnetic recording heads | Ni-Fe | 11 |
| Microelectromechanical systems (MEMS) | Ni | 21 |
| Self-lubricating coatings | Ni-$MoS_2$ | 19,21 |
| Shaped charge liners | Cu | 19 |
| Wear resistant coatings | Ni, Ni-SiC, Ni-P, Co | 11,13,17,19,21,22 |

## Summary

Returning to the key question, "*what nanotechnology really means in the context of metalfinishing?*" many answers have been provided over the past 20 years. It has been shown that electroplating is a technologically feasible approach to produce nanostructured materials with unique physical, chemical and mechanical properties. The outstanding properties of these materials can be understood on the basis of predictable metallurgical nanotechnology principles which have been established over the past several years. Electroplating conditions for the synthesis of these structures using conventional electroplating equipment and chemicals have been established for a wide range of pure metals, alloys and composite materials. Examples of recently developed applications have shown that electrodeposition is an economically viable synthesis route for the large scale manufacture of many different product forms which are difficult to produce with other nanosynthesis methods. Consequently, considerable opportunities exist for the electroplating industries to play a leading role in the development of many emerging and future nanotechnology applications.

## Acknowledgements

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