

Nanotechnology Opportunities for Electroplating Industries

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Nanotechnology is an exciting new field that deals with the design of extremely small structures having critical length dimensions on the order of a few nanometers. Because of the broad field of potential applications, ranging from tiny robots and computers to tissue engineering and completely new materials, this technology has not only captured the attention of researchers and businesses in many different disciplines but also enjoys enormous public interest through widespread coverage in the media, in particular following the recent announcements of substantial government-sponsored nanotechnology initiatives in many countries around the world. This paper deals with nanostructured materials produced by electro-deposition which, over the past decade, have already been advanced from a laboratory-scale phenomenon to a practical materials technology. After presenting some of the fundamentals dealing with synthesis,

structure and properties of electrodeposited nanocrystals, several examples of fully developed and emerging applications of these materials will be discussed. The overall objective of this paper is to help increase the awareness for this rapidly growing field in the electroplating community and to point towards opportunities for this industry.

In recent years, nanotechnology, *i.e.*, the science and technology of controlling and manipulating matter on the nanometer scale, has created tremendous research and business opportunities in many different areas. As a result of the rapidly growing number of examples which demonstrate how materials with exceptional strength, *e.g.*, tiny machines or supercomputers, manipulation of nucleic acid or miniaturization of drug delivery systems and biosensors, can revolutionize our approach to solving problems in engineering, medical and life science applications, it is not surprising that many countries have established comprehensive national and international nanotechnology initiatives. In these programs, substantial funding is provided to support basic and applied research on all aspects of nanotechnology, usually with strong emphasis on interdisciplinary approaches and involving universities, government laboratories and industries.

One particular aspect of nanotechnology deals with nanostructured materials, *i.e.*, materials with ultra-fine crystals, usually less than 100 nm in size, which were initially introduced as interfacial materials about two decades ago.¹ The main structural characteristic of these materials is the enhanced volume fraction of their interface component, *i.e.*, the volume fraction of atoms associated with grain boundaries and triple junctions. As shown in Fig. 1, this volume fraction is negligible in conventional polycrystalline materials. However, it becomes significant at grain sizes of less than 100 nm and exceeds 50% for grain sizes below 10 nm.² Consequently, nanocrystalline materials show considerable changes in many mechanical, physical and chemical properties as a result of having such a large fraction of atoms located at the interfacial defect structure.

Well over 100 different routes for the synthesis of nanostructured materials have been developed in the past few years,³ using one or combinations of several techniques from the following list of processing methods:

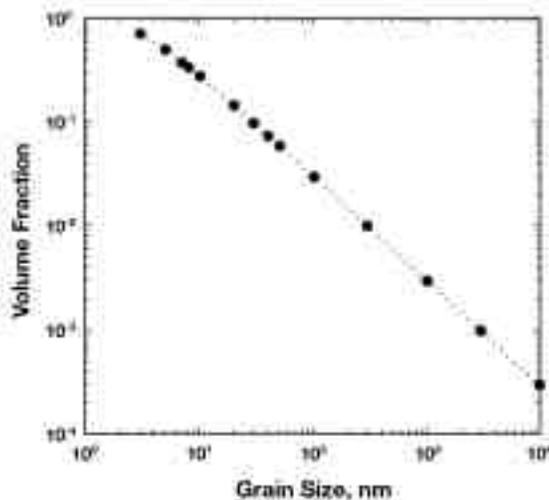


Fig. 1—The effect of grain size on the volume fractions of atoms associated with the interface component (grain boundaries, triple junctions) assuming a grain boundary thickness of 1 nm.

Nuts & Bolts: What This Paper Means to You

This paper is a survey of what is the most exciting area of technology today ... nanotechnology, the deposition of coatings and structures on the scale of nanometers (thousandths of microns). This time around, there are real opportunities for electroplating, which in this case has advantages over vacuum technology. This is so important that the AESF has formed a New Technology Subcommittee in this area. Read on and see what the future has in store.

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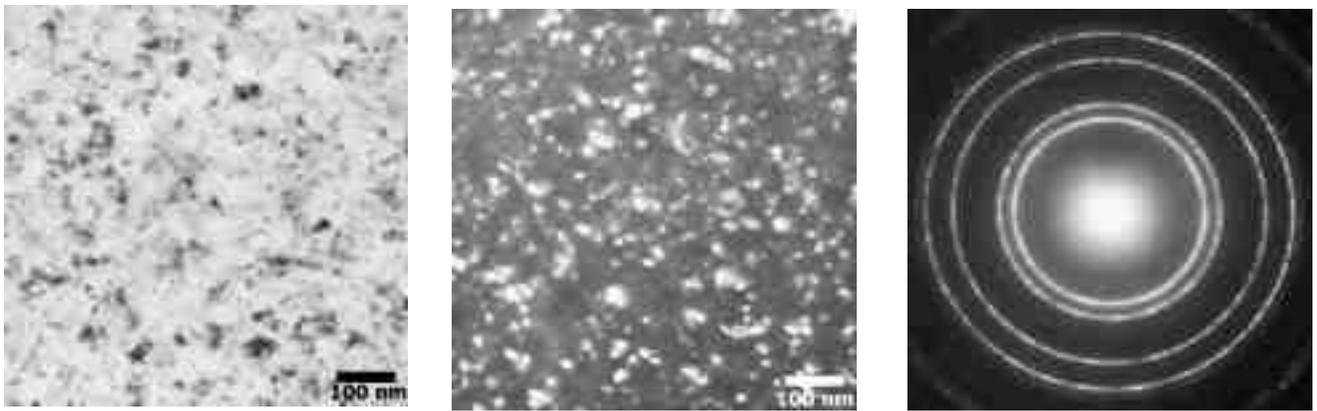


Fig. 2—Transmission electron micrographs (brightfield, darkfield and diffraction pattern) of nanocrystalline nickel produced by pulse electrodeposition from a modified Watts baths following the procedures outlined in Ref. 9.

1. Vapor phase processing (e.g., physical or chemical vapor deposition, inert gas condensation),
2. Liquid phase processing (e.g., rapid solidification, atomization),
3. Solid state processing (e.g., mechanical attrition, crystallization of amorphous precursors),
4. Chemical synthesis (e.g., sol-gel, precipitation) and
5. Electrochemical synthesis (e.g., electrodeposition, electroless deposition).

Many of these techniques operate far from equilibrium conditions so that crystal/grain size is controlled in the nanometer range by favoring nucleation of new grains and reducing the growth of existing grains.

Of particular interest to the community served by AESF are nanostructured materials produced by the electrochemical synthesis routes. Tremendous progress has been made in recent years in the understanding of the basic physical and chemical principles that control nanostructure formation during electrodeposition and electroless deposition. In view of the extensive activities in this field, AESF has recently established a new subcommittee on Nanostructured Materials under the auspices of the Emerging Technologies Committee, which had its inaugural meeting at SUR/FIN® 2002 in Chicago.⁴

This paper addresses the synthesis of nanocrystalline materials by electrodeposition methods as well as structure-property relationships for a variety of nanocrystalline pure metals and alloys. Unlike other techniques, electrodeposition is usually carried out in a single step and produces fully dense materials without the need of a secondary consolidation of powders or the annealing of amorphous precursors. Comparison with structure-property relationships observed for materials produced by other synthesis methods will be given wherever possible. Some emerging industrial applications will also be discussed.

Nanostructured Materials by Electrodeposition

There are numerous early reports in the literature describing electrodeposits with ultra-fine structures.⁵ The first systematic studies on the synthesis of nanocrystalline materials by electrodeposition, in an attempt to optimize certain properties by deliberately controlling the volume fractions of grain boundaries and triple junctions in the material, were published in the late 1980 s.^{6,7} In fact,

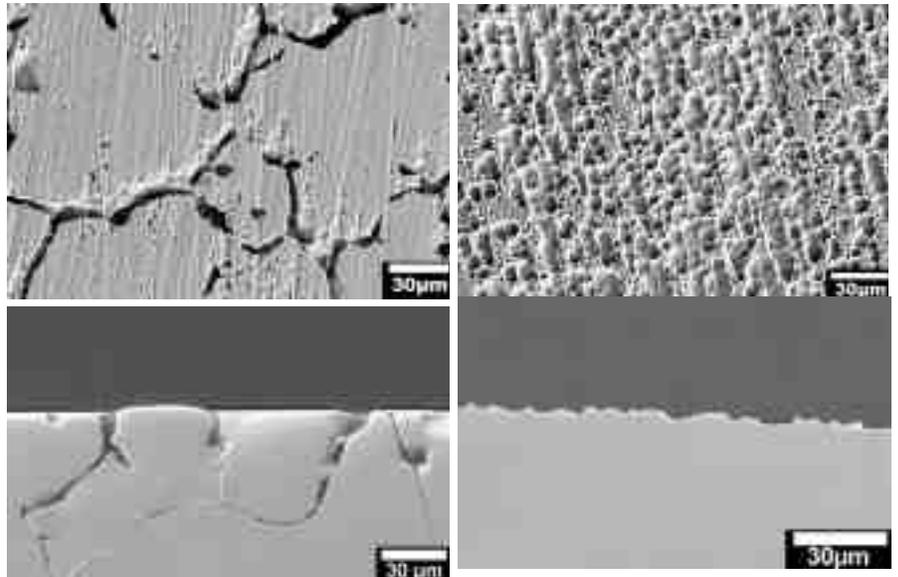


Fig. 3—Top view (top) and cross sectional (bottom) scanning electron micrographs of conventional polycrystalline Ni (left) and nanocrystalline Ni electrodeposits (right) after potentiodynamic polarization in 0.25M Na₂SO₄ solution.⁵⁵

the synthesis of nanostructured materials, with grain size control during the electrodeposition process can be considered a distinct form of grain boundary engineering in which the grain boundary content (types and quantities of grain boundaries) of a material is controlled during material processing to achieve certain physical, chemical and mechanical properties.⁸ The final result is thus a bulk interfacial material, as originally defined by Gleiter,¹ which does not require any further processing of precursor powder material. In this respect electrodeposited nanocrystals are quite different from other nanostructures that are based on consolidated particles.

There are a very large number of pure metals, alloys, composites and ceramics that can be electrodeposited or co-electrodeposited with grain sizes less than 100 nm. The scientific literature reports numerous examples identifying electrochemical processing windows for the synthesis of nanocrystalline pure metals (e.g., Ni,^{9,10} Co,¹¹ Pd,¹² Cu,¹¹) binary alloys (e.g., Ni-P,^{6,7} Ni-Fe,^{13,14} Zn-Ni,^{15,16} Pd-Fe,¹⁷ Co-W,¹⁸) and ternary alloys (e.g., Ni-Fe-Cr¹⁹⁻²¹). Even multi-layered structures or compositionally modulated alloys (e.g., Cu-Pb,²² Cu-Ni,²³⁻²⁵ Ag-Pd,²⁶ Ni-P²⁷), metal matrix composites (e.g., Ni-SiC¹⁰), ceramics (e.g., ZrO₂,²⁸ ZnO²⁹) and ceramic nanocomposites (e.g., Ti_aPb_bO_c³⁰) have been successfully produced by electrodeposition methods. However, the present discussion is limited to equiaxed pure metals and alloys with grain sizes less than 100 nm, without considering grain shape modifications.¹⁹

Additives & Pulse Plating Promote Nanocrystal Formation

Electrocrystallization occurs either by the build up of existing crystals or the formation of new ones.³¹ These two processes are in competition with each other and are influenced by different factors. The two key mechanisms that have been identified as the major rate determining steps for nanocrystal formation are charge transfer at the electrode surface and surface diffusion of adions on the crystal surface.³² One of the key factors in the microstructural evolution of electrodeposits in terms of grain size and shape is inhibition, *e.g.*, resulting from reduced surface diffusion of adions by adsorption of foreign species (such as grain refiners) on the growing surface. A large number of grain refiners have been described in the literature.³³ Their effectiveness depends on surface adsorption characteristics, compatibility with the electrolyte, temperature stability, etc. For example, saccharin,³⁴ coumarin,³⁵ thiourea³⁵ and formic acid³⁶ have all been successfully applied to achieve grain refinement down to the nanocrystalline range for nickel electrodeposits.

The second important factor in nanocrystal formation during electrocrystallization is overpotential.^{31,32} Grain growth is favored at low overpotential and high surface diffusion rates. On the other hand, high overpotential and low diffusion rates promote the formation of new nuclei. These conditions can be experimentally achieved when using pulse plating, where the peak current density can be considerably higher than the limiting current density attained for the same electrolyte during direct current plating.

While many of the processes associated with the crystallization stage are currently not well understood the previous work has shown that electrodeposition will result in nanostructured materials when the plating variables (*e.g.*, bath composition, pH, temperature and current density) are chosen such that electrocrystallization results in massive nucleation and reduced grain growth. An

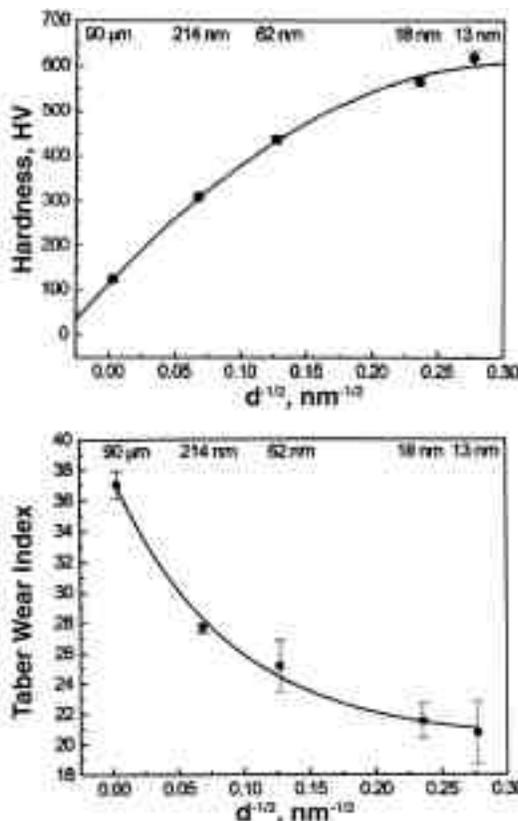


Fig. 4—Hardness (a) and Taber wear index (CS-17 wheel) (b) as function of grain size for Ni.¹⁰¹

unaffected by grain-size changes and includes bulk density,⁶⁷ thermal expansion,^{68,69} Young's modulus,^{45,70-73} resistance to salt spray environment³⁷ and saturation magnetization.^{35,42,52,70,74-79} In the following sections some of these properties are discussed in more detail and comparisons with properties observed in nanostructured materials produced by other methods are made.

Mechanical Properties

The plastic deformation behavior of electrodeposited nanocrystalline materials is strongly dependent on grain size. Much of the early work was concerned with room temperature microhardness measurements on free-standing sheet samples (typical thickness 0.1-0.5 mm) that were initially electrodeposited onto a Ti substrate and then removed from the Ti for hardness measurements. For many nanocrystalline electrodeposits it was shown⁴⁵ that the hardness increases considerably with decreasing grain size, initially following the well-established Hall-Petch relationship. For example, for nanocrystalline Ni the Vickers hardness increased from 120 VHN at a grain size of 100 μm to more than 650 VHN at a grain size of about 10 nm. However, for even smaller grain sizes (6 nm) a slight reduction in the hardness to about 590 VHN was observed. This unexpected behavior, often referred to as the inverse Hall-Petch relationship, also was observed in nanocrystalline materials produced by other synthesis methods, *e.g.*, the inert gas condensation technique,⁸¹ while others⁸² have only observed a reduction in the Hall-Petch slope, but no clear transition to inverse Hall-Petch behavior.

A more complete study on mechanical properties of nanocrystalline materials was performed in conjunction with the development of the first large-scale industrial application of electrodeposited nanocrystalline materials.^{47,48,8} The results of various mechanical

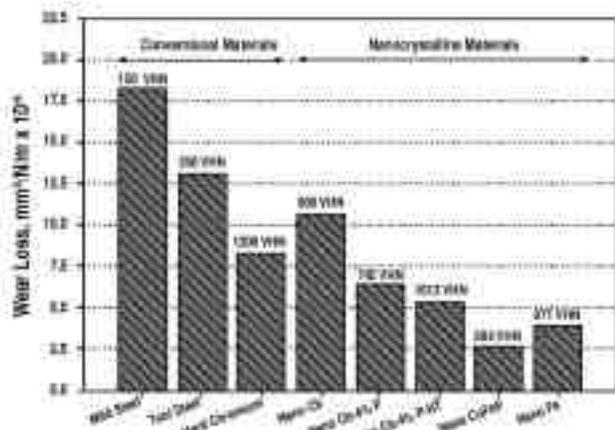


Fig. 5—Pin-on-disk (POD) wear loss values for various nanocrystalline materials along with mild steel, tool steel and hard chromium. The Vickers microhardness value (VHN) is given on top of the bar for each material on the chart.¹⁰⁰

example of a pulse plated Ni sample is shown in Fig. 2. Under these conditions the effect of the substrate on the resulting bulk electrodeposit often becomes negligible.³⁷

Electrodeposition of nanocrystalline materials is not limited to coating applications. As will be discussed in more detail below, it can also be used as a cost-effective method in the production of free-standing forms such as ultra-thin foil, wire, sheet and plate as well as complex shapes.

Properties of Nanostructures

A critical assessment of the properties measured to date on electrodeposited nanocrystals shows that these can be classified into two categories. The first group of properties is strongly dependent on grain size. These properties include strength, ductility and hardness,^{14,21,38-49} wear resistance and coefficient of friction,⁵⁰ electrical resistivity,^{11,51} coercivity,⁵² hydrogen solubility and diffusivity,⁵³ resistance to localized corrosion and intergranular stress corrosion cracking^{47,48,54-58} and thermal stability.^{38,44,47,48,59-66} The other group of properties is relatively

properties of nanocrystalline nickel with grain sizes of 10 nm and 100 nm as compared to conventional polycrystalline materials are shown in the table. In addition to the remarkable increases in hardness, yield strength and ultimate tensile strength with decreasing grain size, it is interesting to note that the work hardening coefficient decreases with decreasing grain size to virtually zero at a grain size of 10 nm. In tensile tests the ductility of the material was found to decrease with decreasing grain size from 50% elongation to failure for conventional material to 15% at 100 nm grain size and about 1% at 10 nm grain size. Generally, somewhat greater ductility was observed in bending. A slight recovery in tensile ductility was observed for grain sizes less than 10 nm.⁴⁹ Considerably higher ductility was recently observed for nanocrystalline cobalt electrodeposits. That at 12 nm grain size, displayed strain to failure values of 8-10% at a remarkable tensile strength of 1860 MPa, compared to 10% ductility for polycrystalline Co (5 μm grain size) with 800 MPa tensile strength.⁸³

Corrosion Properties of Nanocrystalline Metals & Alloys

The corrosion resistance of nanocrystalline materials in aqueous solutions is of great importance in assessing a wide range of potential future applications. To date research in this area is still scarce and relatively few studies have addressed this issue. In the case of the corrosion behavior of nanocrystalline materials produced by crystallization of amorphous precursor materials⁸⁴⁻⁸⁸ both beneficial and detrimental effects of the nanostructure formation on the corrosion performance were observed. The conflicting results to a large extent are due to the poorly characterized microstructures of the crystallized amorphous materials. On the other hand, for nanostructured materials produced by electrodeposition, considerable advances in the understanding of the effect of the microstructure on the corrosion properties have been made in recent years.^{47,48,55-58}

Electrochemical studies of nanocrystalline Ni,⁵⁴⁻⁵⁶ have shown that when compared to polycrystalline nickel, the material shows slightly higher general corrosion rates but a reduced tendency to localized corrosion. Figure 3 shows planar and cross-sectional scanning electron micrographs of polycrystalline and nanocrystalline nickel after potentiodynamic testing in a 0.25M Na_2SO_4 solutions. Both specimens exhibit corrosion damage but the nanocrystalline Ni is more uniformly corroded while the specimen with 100 μm grain size shows extensive localized attack along the grain boundaries and triple junctions resulting in excessive material loss due to grain dropping. X-ray photoelectron spectroscopy of similar specimens corroded in 2N H_2SO_4 solution showed that the passive film formed on the nanostructured specimen is more defective than that formed on the polycrystalline specimen while the thickness of the passive layer was the same on both specimens.⁸⁹ This more highly defective film on the nanocrystalline specimen allows for a more uniform breakdown of the passive film, which in turn leads to more uniform corrosion. In contrast, as has

Table 1
Mechanical Properties of Conventional & Nanocrystalline Nickel

Property	Conventional***	Nano-Ni 100nm	Nano-Ni 10 nm
Yield Strength, MPa (25°C; 77°F)	103	690	>900
Yield Strength, MPa (350°C; 662°F)	---	620	---
Ultimate Tensile Strength, MPa (25°C; 77°F)	403	1100	>2000
Ultimate Tensile Strength, MPa (350°C; 662°F)	---	760	---
Tensile Elongation, % (25°C; 77°F)	50	>15	1
Elongation in Bending, % (25°C; 77°F)	---	>40	---
Modulus of Elasticity, GPa (25°C; 77°F)	207	214	204
Vickers Hardness, kg/mm ²	140	300	650
Working Hardening Coefficient	0.4	0.15	0.0
Fatigue Strength, MPa (10 ⁸ cycles / air (25°C; 77°F)	241	275	---
Wear rate (Dry air pin-on-disc), $\mu\text{m}^3/\mu\text{m}$	1330	---	7.9
Coeff. of friction (dry air pin-on-disc)	0.9	---	0.5

***ASM Metals Handbook, Vol. 2, ASM International, Metals Park, OH, 1993; p. 437.

been previously shown, in coarse-grained Ni the breakdown of the passive film occurs first at the grain boundaries and triple junctions rather than the crystal surface, leading to preferential attack at these defects.⁹⁰

More recently the corrosion behavior of nanocrystalline Ni was also studied in 30 wt% KOH solution⁵⁸ and pH neutral solution containing 3 wt% sodium chloride.⁹¹ The results were similar to the corrosion behavior observed in sulfuric acid. The general corrosion was somewhat enhanced compared to conventional polycrystalline Ni. However, the nanostructured materials were much more immune to localized attack, which often can lead to catastrophic failures.

Using the ASTM B-117 salt spray test it was found that the microstructure of Ni has little effect on the overall corrosion performance under these electrochemical conditions.³⁷ Both conventional polycrystalline and nanostructured coatings gave the same corrosion protection to mild steel substrates.

Further corrosion testing was performed on nanocrystalline Ni under conditions required for steam generator alloy application.⁴⁷ The results showed that electrodeposited nanostructured Ni with a grain size of 100 nm is intrinsically resistant to intergranular processes such as intergranular attack and intergranular stress corrosion cracking. The material was found to be resistant to pitting attack and only slightly susceptible to crevice corrosion. Excellent corrosion performance was also reported for nanocrystalline Zn-Ni⁹² and Co⁹³ electrodeposits.

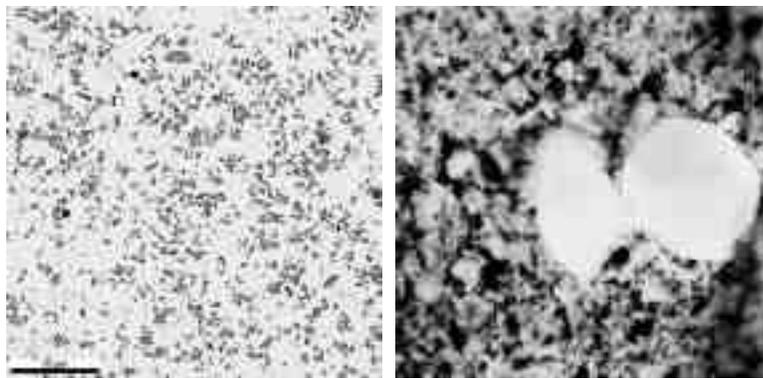


Fig. 6—(a) Backscattered scanning electron micrograph of nanocrystalline nickel matrix (20 nm average grain size) containing Al_2O_3 particulates (black), (b) bright field TEM micrograph of same deposit showing the interface between the matrix and the Al_2O_3 particles.

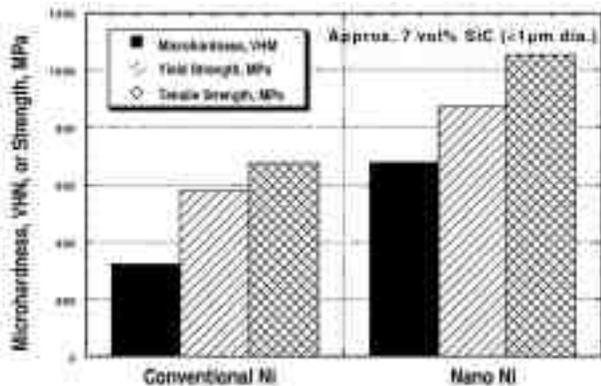


Fig. 7—Summary of mechanical properties for nickel/silicon carbide composites for conventional and nanocrystalline Ni matrices produced by electrodeposition.¹⁰²

Thermal Stability of Nanostructured Metals & Alloys

Of particular importance for any nanocrystalline material is its thermal stability. From an applications point of view, it is the onset of grain growth that ultimately limits the temperature range in which these materials can be used in service. A comprehensive summary of studies on the thermal stability of nanocrystalline electrodeposits is available.⁹⁴ In this section we discuss some of the critical issues associated with grain growth in these materials.

In an early study the grain growth kinetics of a nanocrystalline Ni-1.2 wt% P alloy with a starting grain size of 10 nm was evaluated from *in-situ* electron microscopy observations.⁵⁹ At 200°C (392°F), no grain growth was observed and the material was stable as a solid solution. At 400°C (752°F), substantial grain growth was observed within the first few minutes of annealing, resulting in a microcrystalline two phase (Ni + Ni₃P) structure. However, at 300 and 400°C (572 and 752°F) the grain size initially increased rapidly by a factor of 2-3 and then became essentially independent of annealing time. Similar behavior was observed for a Ni-S alloy at 300°C (572°F).⁶¹

Grain growth kinetics leading to a constant characteristic grain size is common for systems subjected to large grain boundary dragging forces. Considering the extremely large driving forces for grain growth expected in these materials (*e.g.*, about 200 J/cm³ at a grain size of 20 nm⁶⁰), the observed thermal stabilization may not be attributed solely to such a mechanism. In nanocrystalline materials an additional dragging force may be due to triple junctions.⁵⁹ It has been shown that grain growth in fine-grained polycrystalline materials may be controlled by the intrinsic mobility of triple junctions.⁹⁵ A further contribution of triple junctions to the thermal stability of nanostructured materials is the result of preferential

solute segregation to these sites.⁹⁶ Such solute enrichment at triple junctions in annealed nanostructured Ni-0.12 wt% S was recently observed by EDX measurements with a dedicated scanning transmission microscopy.⁶³

The beneficial effect of microalloying on the thermal stability has been further demonstrated for nanocrystalline nickel (approximately 100 nm grain size).^{47,48} In this case the thermal stability was assessed indirectly by measuring the hardness of pure nanocrystalline Ni and nanocrystalline Ni-P (<3000 ppm P) annealed at 343°C (649°F) as a function of annealing time. For pure nanocrystalline Ni the hardness decreased rapidly from about 420 VHN to 150 VHN within the first 100 minutes of annealing. However, for nanocrystalline Ni-P the hardness remained unchanged at 420 VHN for annealing times of in excess of 10⁶ minutes. In this case, the thermal stability of microalloyed Ni was attributed mainly to solute drag and possible Zener drag by microprecipitates.

A recent theoretical and experimental study⁹⁷ on the effect of grain growth on resultant grain boundary character distributions indicates that the thermal stability of nanocrystalline materials may be further enhanced by the tendency for these ultra-fine grained materials to form “special” low-energy grain boundaries during the early stages of grain growth.



Fig. 8—Self-lubricating nanocrystalline nickel + molybdenum disulfide composite coating on hydraulic expansion mandrels.

Electrical Properties

A comparison of results of electrical property measurements performed on nanostructured materials produced by different synthesis routes (*e.g.*, gas condensation,⁹⁸ electrodeposition^{11,51,99}) shows that for all nanocrystalline metals the electrical resistivity increases with decreasing grain size. For example, the room temperature resistivity for Ni was increased from about 6 μ-cm at 100 μm grain size in fully annealed material, to about 22 μ-cm at 11 nm grain size in electrodeposited material.⁵¹

This can be attributed to electron scattering at defects, such as grain boundaries and triple junctions. In fact, a more comprehensive study⁹⁹ has recently shown that the contribution of the grain boundaries to the electrical resistivity in nanocrystalline electrodeposits can be quantified in terms of a specific grain boundary resistivity. The temperature coefficient of resistivity also behaves similarly for materials produced by different synthesis routes. Both nanocrystalline materials produced by inert gas condensation⁹⁸ and electrodeposited Ni^{51,99} and Co^{11,99} show decreasing values with decreasing grain size.

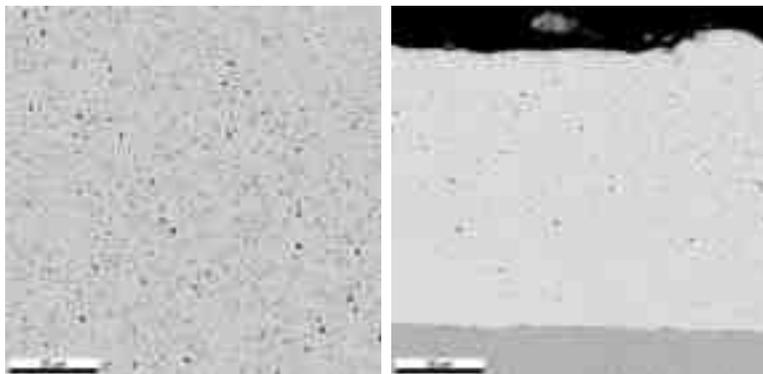


Fig. 9—Parallel (a) and through-thickness (b) SEM micrographs of a nanocrystalline Ni-P matrix with BN particles.

Wear Properties

Hardfacing coatings see extensive use in numerous industrial applications. These coatings require a high intrinsic hardness (600-1000 VHN) and low friction coefficient (<0.20) in order to impart the desirable wear performance. Electrodeposited nanocrystalline metal and alloy coatings display properties such as hardness and ductility that may make them excellent hardfacing material.^{100,101}

Figure 4 shows the effect of average grain size on both the hardness and Taber Wear Index (a measure of volume loss due to abrasive wear) for nickel. As shown, decreasing the grain size of Ni from 90 μm to 13 nm results in hardness increases from 125 to 625 VHN; commensurately, the Taber Wear Index (using a CS—17 wheel) is reduced from approximately 37 to 21.

Figure 5 shows the Pin-on-Disk (POD) volumetric wear loss for various nanocrystalline Co alloys relative to those obtained with mild steel, tool steel and hard chromium that are commonly used for hardfacing applications. As noted in this figure, the wear resistance is no longer a simple function of the material hardness. When tested under identical conditions, the wear resistance of most of the nanocrystalline deposits exceeded that of hard chromium, even though their hardness values were lower. The POD volumetric wear loss values for nanocrystalline cobalt decrease with the addition of phosphorus and with precipitation hardening. The addition of iron results in a further decrease in the wear loss.

Further increases in hardness, and wear resistance may be achievable through the incorporation of second phase particulates in the nanocrystalline metal/alloy matrix. One approach is alloy deposition followed by heat treatment to precipitate a finely dispersed second phase.

Nanocomposite coatings can also be produced by co-deposition, whereby the second phase particulate is kept in suspension in the plating bath. In this manner, insoluble second phases of metal, alloy, ceramic or polymer can be uniformly distributed in the host nanocrystalline metal or alloy matrix. Figure 6a shows an example of nanocrystalline nickel (13 nm avg. grain size) containing a uniform dispersion of aluminum oxide particles (approx. 1 μm in diameter), produced by electrodeposition. Figure 6b presents a bright field TEM image of two Al_2O_3 particles and the surrounding nanocrystalline matrix showing that the nanocrystalline matrix structure continues up to the particle/matrix interface.

The benefit of utilizing a nanocrystalline metal-ceramic composite is shown in Figure 7 for Ni + SiC. Significant increases in hardness, yield strength and ultimate tensile strength are achieved by utilizing a nanocrystalline rather than a conventional nickel matrix. In this work,¹⁰² it was noted also that the nanocrystalline composite possessed significantly improved ductility compared with nanocrystalline Ni without SiC.

The incorporation of second phase particles offers the opportunity to tailor specific functional properties. For example, hard-facing coatings with self-lubricating properties are highly desirable in certain applications. Such properties could be achieved through the use of dry lubricant particles such as graphite and PTFE. Such co-deposited systems are already commercially available with a conventional grain size matrix (e.g., Ni). However, the use of a hard, nanocrystalline matrix extends the applicability of these coatings to more severe industrial applications because, by application of the rule of mixtures, the relatively “soft” lubricating second phase can be incorporated to larger volume fractions without significant compromise of the overall hardness of the coating. Figure 8 shows a photograph of hydraulic expansion mandrels, coated with a nanocrystalline Ni-MoS₂ composite, which utilize the self-lubricating mechanism in order to extend their service life.

Figures 9a and b show planar and through-thickness SEM micrographs, respectively, of a nanocrystalline Ni-P matrix containing hexagonal boron nitride (BN) particles (mean particle size $\sim 10 \mu\text{m}$). The presence of the BN particles in the material results in a coating that “self-lubricates” during wear.

Grain Size—Independent Properties

Grain size has little effect on the saturation magnetization, thermal expansion and heat capacity of nickel produced by electrodeposition as shown in Figure 10.¹⁰³ Another property that is constant for nano- and microcrystalline metals is Young's modulus. These results are in strong

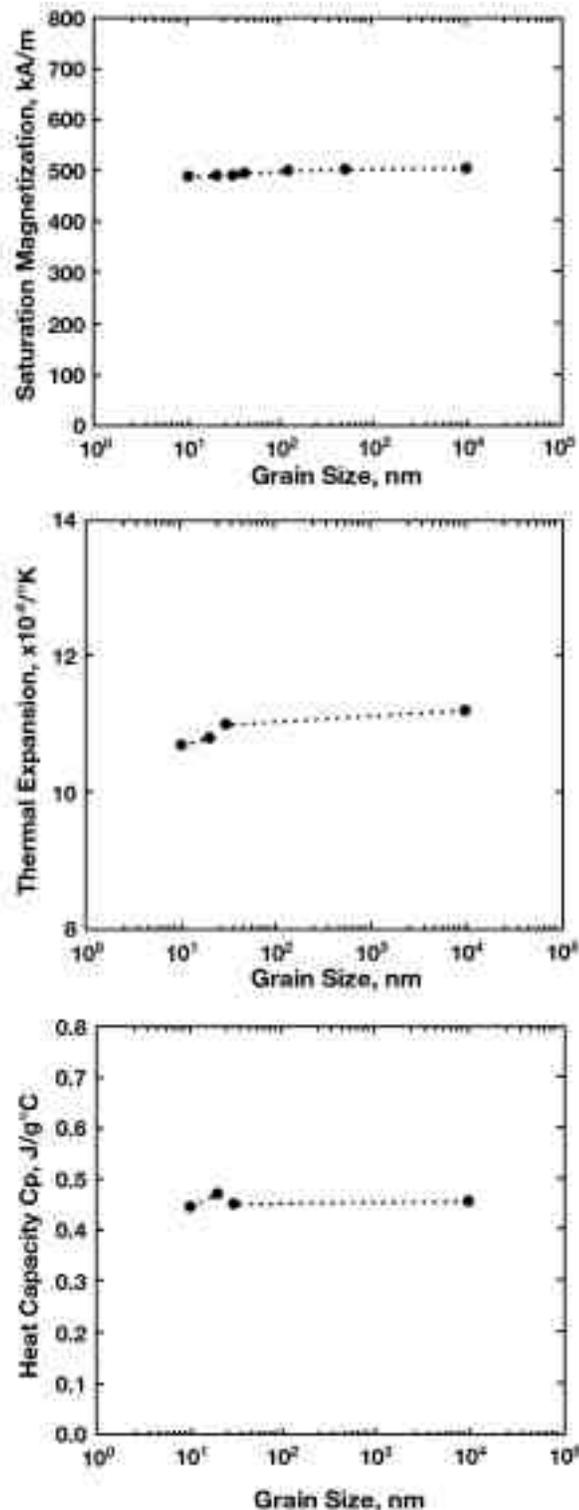


Fig. 10—Grain size dependence of saturation magnetization, thermal expansion and heat capacity of nickel at room temperature.

disagreement with earlier reports for nanocrystalline materials that were produced by consolidation of precursor powders (See Ref. 72 for further discussion.), which showed major reductions for these properties with decreasing grain size.

Theoretical analysis of the effect of grain size reduction and its impact on the material defects and structural disorder have shown that grain size should have little effect on the properties addressed above,^{73,78} at least in the grain size range from 10 to 100 nm. These studies and further experimental evidence clearly show that the previously observed strong grain size dependence of these properties stem from internal porosity and associated impurities and/or internal oxidation effects. More recent results of materials produced by powder consolidation, but with low residual porosity, are comparable with those of the electrodeposited, fully dense equivalent material.

Applications

Electrodeposited nanostructures have advanced rapidly to commercial application as a result of (1) an established industrial infrastructure (*i.e.*, electroplating and electroforming industries), (2) a relatively low cost of application whereby nanomaterials can be produced by simple modification of bath chemistries and electrical parameters used in current plating and electroforming operations, (3) the capability in a single-step process to produce metals, alloys and metal-matrix composites in various forms (*i.e.*, coatings, free-standing complex shapes), and most importantly (4) the ability to produce *fully dense* nanostructures free of extraneous porosity. The importance of the latter cannot be overemphasized with regard to industrial application because, as has been outlined in previous sections, many of the unusual properties initially attributed to nanostructures have since been demonstrated to be an artifact of residual porosity in these materials. From the outset, the fully dense nanomaterials produced by electrodeposition have displayed *predictable* material properties based upon their increased content of intercrystalline defects. This “predictability” in ultimate material performance has accelerated the adoption of nanomaterials by industry, whereby such extreme grain refinement simply represents another metallurgical tool for microstructural optimization. It is important to note the importance of property-specific grain size “optimization” rather than grain miniaturization for its own sake since different properties scale differently with grain size.

Structural Applications

As would be expected from Hall-Petch considerations, numerous practical applications for nanocrystalline materials are based upon opportunities for high strength coatings and free-standing structural components. The superior mechanical properties of these electrodeposited nanostructures have led to one of their first large scale industrial applications for *in-situ* repair of nuclear steam generator tubing.^{47,48,99} This proprietary process¹⁰⁴ has been successfully implemented in both nuclear Canadian CANDU and U.S. pressurized water reactors, and has been incorporated as a standard procedure for pressure tubing repair.¹⁰⁵ In this application,

⁹⁹Electrosleeve® Process, Framatone Technologies, Inc., Lynchburg, VA. [www.framatech.com].

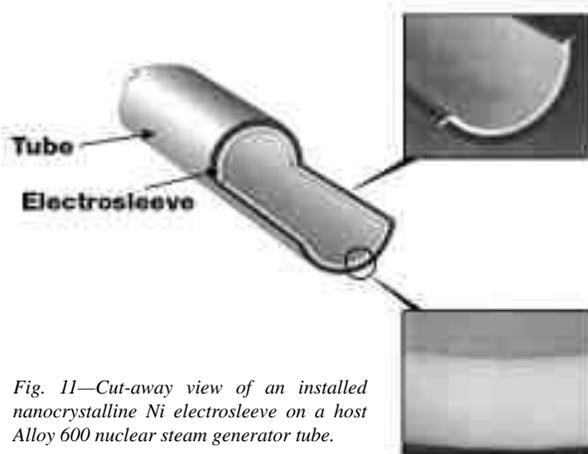


Fig. 11—Cut-away view of an installed nanocrystalline Ni electro-sleeve on a host Alloy 600 nuclear steam generator tube.

a nanocrystalline Ni-P microalloy (grain size approximately 100 nm) is electrodeposited on the inside surface of steam generator tubes to a thickness that ranges from 0.5 to 1 mm to structurally repair those sites in the tubes where the original structural integrity has been compromised (*e.g.*, localized corrosion, stress corrosion cracking, etc.). Figure 11 shows a cut-away view of the results. The high strength, good ductility and thermal stability [up to 400° (752°F)] of this nanocrystalline material permits the use of a much thinner “sleeve” (0.5-1.0 mm) than if a polycrystalline

material is used. The low thickness of the repair also minimizes the impact on fluid flow and heat transfer in the steam generator. The first installations were done in 1994 in a CANDU unit and in 1999 in a PWR unit. Their performance to date has met all expectations.

Recent geometric models and experimental findings^{106,107} have shown that nanostructured materials can also possess a high resistance to intergranular cracking processes, including creep cracking. Several emerging applications for nanocrystalline materials possessing high intergranular cracking resistance include, lead-acid battery (positive) grids and shaped charge liners (Cu, Pb, Ni) for military and industrial applications (*e.g.*, demolition, oil well penetrators, etc.). These are applications in which durability and performance are frequently compromised by premature intergranular failure.

Functional Applications

A major application for drum-plated nanocrystalline material is in the production of copper foil for printed circuit boards, where enhanced etching rates and reduced line spacing/pitch can be achieved by reducing grain size. Grain size can be optimized on the basis of calculated electrical resistivity for nanocrystalline Cu,⁹⁹ as summarized in Fig. 12. A 50 to 100 nm grain size provides optimum etchability while maintaining good electrical conductivity.

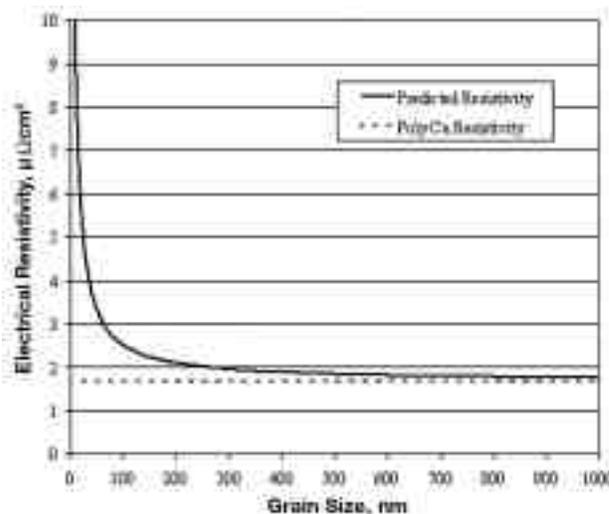


Fig. 12—Calculated room temperature electrical resistivity of Cu as a function of grain size.⁹⁹

Coating Applications

The improved hardness, wear resistance and corrosion resistance, coupled with undiminished saturation magnetization and predictable thermal expansion, elastic properties and electrical resistivity, make nanocrystalline coatings ideal candidates for protective and functional applications (*e.g.*, as used in hard facing on softer, less wear resistant coatings, recording heads, electronic connectors, replacement coatings for chromium and cadmium in automotive and aerospace applications). For applications as thin coatings (in the order of a few μm thick) the microstructural evolution of the deposit with increasing coating thickness can be a major concern. Many previous studies on conventional electrodeposits have shown that the grain size usually increases considerably with increasing coating thickness.¹⁰⁸ In contrast, nanocrystalline Ni electrodeposits⁹ showed that in most cases the nanostructure was fully established right at the interface with the substrate and that the grain size was essentially independent of coating thickness.¹⁰⁹ For certain electrochemical and substrate conditions a thin transition layer of larger grains was observed in which the initial structure was influenced by the larger grains of the substrate, presumably by an epitaxy mechanism. However, even in this case a constant, thickness-independent structure was fully established within the first 200 nm from the interface.

Nanocrystalline Materials As a Chromium Replacement

The most widely applied hard facing coating is electrodeposited chromium (5 to 250 μm thick), which continues to be used extensively in both industrial and military applications. Hexavalent chromic acid baths are normally used to electrodeposit hard chromium. However, health risks associated with the use of hexavalent chromium baths have been recognized since the early 1930s. Although significant progress has been made in the development of less harmful trivalent chromium plating processes, a reliable industrial process has yet to emerge. In addition to the health risks associated with hexavalent Cr plating, there are several other technical drawbacks to this technology. As a result of the relatively low electrolytic efficiency of Cr plating processes, deposition (or build) rates are relatively low compared to the plating of other metals and alloys (*e.g.*, 25–50 $\mu\text{m}/\text{h}$ for Cr versus $> 200 \mu\text{m}/\text{h}$ for nickel). As a further consequence of this low plating efficiency, high rates of hydrogen co-generation occur and precautions must be taken to prevent hydrogen embrittlement of susceptible substrate materials (*e.g.*, high strength steels). Moreover, the intrinsic brittleness of hard chromium deposits (*i.e.*, $< 0.1\%$ tensile elongation) invariably leads to micro- or macro-cracked deposits. These cracks, which do not compromise wear and erosion resistance, are wholly unsuitable for applications where corrosion and fatigue resistance is required.

Electrodeposited nanocrystalline metal and alloy coatings, possessing extreme grain refinement to the 3–100 nm size range, in addition to being fully compatible with current hard chromium plating infrastructure, have displayed properties that may render them a superior alternative to hard chromium coating technology. It is important to note that there exist other significant benefits possessed by these nanocrystalline coatings for specific applications. For example, the higher ductility of the nanocrystalline materials relative to hard chromium, and the absence of microcracking, provides significant advantages in fatigue and corrosion performance. Also, the high current efficiencies associated with the deposition of these nanocrystalline materials mitigate problems associated with hydrogen embrittlement. Additionally, nanocrystalline single-phase systems can provide a hard but ductile matrix for incorpora-

tion of second phase particles that can impart even greater hard-facing improvements.

Nanocrystalline cobalt, cobalt-phosphorus and cobalt-iron alloys have been shown to have microhardness values in same range as hard chromium, while maintaining considerable ductility and high plating efficiency. The Taber wear resistance of nanocrystalline cobalt-iron alloys approaches that of hard chromium, while possessing lower hardness values. Further alloying of nanocrystalline cobalt-iron with phosphorus may increase the as-deposited hardness thus increasing the wear resistance to values matching and/or exceeding hard chromium.¹¹⁰

Conclusions

Electrodeposition has been shown to be a technologically feasible approach to produce nanostructured materials with unique physical, chemical and mechanical properties. Electroplating windows 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 systems. Examples of recently developed applications have shown that electrodeposition is an economically viable synthesis route for the manufacture of many different product forms ranging from thin and thick coatings, freestanding foil and plate, to complex electroformed shapes. Consequently, considerable opportunities exist for the electroplating industry to play a leading role in the development of many new nanotechnology applications, which can be readily implemented based on predictable metallurgical nanotechnology principles established over the past several years.

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References

1. H. Gleiter, in "Deformation of Polycrystals: Mechanisms and Microstructures," *Proc. 2nd Risø Int. Symp. on Metallurgy and Materials Science*, Risø National Laboratory, Roskilde Denmark, 1991; p. 15.
2. G. Palumbo, S.J. Thorpe & K.T. Aust, *Scripta Metall. et Mater.*, **24**, 1347 (1990).
3. "Proc. 5th Int. Conf. on Nanostructural Materials (NANO 2000)" in *Scripta Mater.*, **44**, 1161 (2001).
4. *Plating and Surface Finishing*, **89**, 8 (September 2002).
5. A. Brenner, *Electrodeposition of Alloys: Principles and Practice*, Academic Press, New York, 1963.
6. G. McMahon & U. Erb, *Microstr. Sci.*, **17**, 447 (1989).
7. G. McMahon & U. Erb, *J. Mat. Sci. Lett.*, **8**, 865 (1989).
8. K.T. Aust, U. Erb & G. Palumbo, in "Mechanical Properties and Deformation Behaviour of Materials Having Ultrafine Microstructures", M. Nastasi, *et al.* (eds), Kluwer Academic Publishers, 1993; p. 107.
9. U. Erb & A.M. El-Sherik, U.S. patent 5,352,266 (1994).
10. U. Erb, A.M. El-Sherik, G. Palumbo & K.T. Aust, *Nanostructural Materials*, **2**, 383 (1993).
11. I. Bakonyi, E. Toth-Kadar, J. Toth, T. Tarnoczi and A. Cziraki, in "Processing and Properties of Nanocrystalline Materials", C. Suryanarayana, *et al.* (eds.), TMS, Warrendale, PA, 1996; p. 465.

12. R. Würschum, S. Gruss, B. Gissibl, H. Natter, R. Hempelmann & H.E. Schäfer, *Nanostructural Materials*, **9**, 615 (1997).
13. D.L. Grimmett, Ph.D. Thesis, University of California - Los Angeles, 1988.
14. C. Cheung, F. Djuanda, U. Erb & G. Palumbo, *Nanostructural Materials*, **5**, 513 (1995).
15. A.M. Alfantazi, A.M. El-Sherik & U. Erb, *Scripta Metall. et Mater.*, **30**, 1245 (1994).
16. A.M. Alfantazi & U. Erb, *J. Mat. Sci. Lett.*, **15**, 1361 (1996).
17. K.J. Bryden & J.Y. Ying, *Nanostructural Materials*, **9**, 485 (1997).
18. D. Osmola, E. Renaud, U. Erb, L. Wong, G. Palumbo & K.T. Aust, *Proc. Mat. Res. Soc. Symp.*, **286**, 161 (1993).
19. C. Cheung, U. Erb & G. Palumbo, *Mat. Sci. Eng.*, **A185**, **39** (1994).
20. C. Cheung, P. Nolan & U. Erb, *Mat. Lett.*, **20**, 135 (1994).
21. C. Cheung, G. Palumbo & U. Erb, *Scripta Metall. et Mater.*, **31**, 735 (1994).
22. A.R. Despic & V.D. Jovic, *J. Electrochem. Soc.*, **134**, 3004 (1987).
23. D.S. Lashmore & M.P. Dariel, *J. Electrochem. Soc.*, **135**, 1218 (1988).
24. D. Tench & J. White, *Metall. Trans.*, **15A**, 2039 (1994).
25. J. Yahalom & O. Zadok, *J. Mat. Sci.*, **22**, 499 (1987).
26. U. Cohen, F.B. Koch & R. Sand, *J. Electrochem. Soc.*, **130**, 1987 (1983).
27. A. Haseeb, B. Blanpain, G. Wouters, J.P. Celis & J.R. Roos, *J. Mat. Sci. Eng.*, **A168**, 137 (1993).
28. M. Shirkhazadeh, *Mat. Lett.*, **16**, 189 (1993).
29. A. Dierstein, H. Natter, F. Meyer, H. Stephan, C. Kropf & R. Hempelmann, *Scripta Mater.*, **44**, 2209 (2001).
30. J.A. Switzer, *Nanostructural Materials*, **1**, 43 (1992).
31. J.O.M. Bockris & G.A. Razumney, *Fundamental Aspects of Electrocrystallization*, Plenum Press, New York, NY, 1967; p. 27.
32. R.T.C. Choo, A.M. El-Sherik, J. Toguri & U. Erb, *J. Appl. Electrochem.*, **25**, 384 (1995).
33. J.W. Dini, *Electrodeposition*, Noyes Publications, Park Ridge, N J, 1993.
34. A.M. El-Sherik & U. Erb, *J. Mat. Sci.*, **30**, 5743 (1995).
35. U. Erb, A.M. El-Sherik, C.K.S. Cheung & M. Aus, U.S. patent 5,433,797 (1995).
36. A. Cziraki, B. Fogarassi, I. Gerocs, E. Toth-Kadar & I. Bakonyi, *J. Mat. Sci.*, **29**, 4771 (1994).
37. A.M. El-Sherik & U. Erb, *Plating and Surface Finishing*, **82**, 85 (September 1995).
38. G. Palumbo, K.T. Aust & U. Erb, *Mat. Sci. Forum*, **225-227**, 281 (1996).
39. G. Palumbo, U. Erb & K.T. Aust, *Scripta Metall. et Mater.*, **24**, 2347 (1990).
40. A.M. El-Sherik, U. Erb, G. Palumbo & K.T. Aust, *Scripta Metall. et Mater.*, **27**, 1185 (1992).
41. L. Wong, D. Ostrander, U. Erb, G. Palumbo & K.T. Aust, in *Nanophases and Nanocrystalline Structures*, R.D. Shull and J.M. Sanchez (eds.), TMS, Warrendale, PA, 1994; p. 85.
42. R. Rofagha & U. Erb, in *Defect Structure, Morphology and Properties of Deposits*, H. Merchant (ed.), TMS, Warrendale, PA, 1995; p. 245.
43. N. Wang, Z. Wang, K.T. Aust & U. Erb, *Acta Metall. et Mater.*, **43**, 519 (1995).
44. A.M. Alfantazi & U. Erb, *Mat. Sci. Eng.*, **A212**, 123 (1996).
45. U. Erb, G. Palumbo, R. Zugic & K.T. Aust, in *Processing and Properties of Nanocrystalline Materials*, C. Suryanarayana, et al. (eds.), TMS, Warrendale, PA, 1996; p. 93.
46. K.T. Aust, U. Erb & G. Palumbo, in *Processing and Properties of Nanocrystalline Materials*, C. Suryanarayana, et al. (eds.), TMS, Warrendale, PA, 1996; p. 11.
47. F. Gonzalez, A.M. Brennenstuhl, G. Palumbo, U. Erb & P.C. Lichtenberger, *Mat. Sci. Forum*, **225-227**, 831 (1996).
48. G. Palumbo, F. Gonzalez, A.M. Brennenstuhl, U. Erb, W. Shmayda & P.C. Lichtenberger, *Nanostructural Materials*, **9**, 737 (1997).
49. N. Wang, Z. Wang, K.T. Aust & U. Erb, *Mat. Sci. Eng.*, **A237**, 150 (1997).
50. A.M. El-Sherik & U. Erb, in *Nickel-Cobalt 97: Volume IV, Applications and Materials Performance*, F.N. Smith, et al. (eds.), The Metallurgical Society of CIM, Montreal, PQ, 1997; p. 257.
51. M.J. Aus, B. Szpunar, U. Erb, A.M. El-Sherik, G. Palumbo & K.T. Aust, *J. Appl. Phys.*, **75**, 3632 (1994).
52. M.J. Aus, B. Szpunar, A.M. El-Sherik, U. Erb, G. Palumbo & K.T. Aust, *Scripta Metall. et Mater.*, **27**, 163 (1992).
53. D.M. Doyle, G. Palumbo, K.T. Aust, A.M. El-Sherik & U. Erb, *Acta Metall. et Mater.*, **43**, 3027 (1995).
54. R. Rofagha, R. Langer, A.M. El-Sherik, U. Erb, G. Palumbo & K.T. Aust, *Scripta Metall. et Mater.*, **25**, 2867 (1991).
55. S. Kim, K.T. Aust, U. Erb, G. Ogundele & F. Gonzalez, *Proc. AESF SUR/FIN 2002*, AESF, Orlando, FL, 2002; p. 975.
56. S. Kim, F. Gonzalez, G. Panagiotopoulos, G. Palumbo, U. Erb & K.T. Aust, *Proc. AESF SUR/FIN® 2001*, AESF, Orlando, FL, 2001; p. 159.
57. R. Rofagha, U. Erb, D. Ostrander, G. Palumbo & K.T. Aust, *Nanostructural Materials*, **2**, 1 (1993).
58. S. Wang, R. Rofagha, P.R. Roberge & U. Erb, *Proc. Electrochem. Soc.*, **95-8**, 224 (1995).
59. K. Boylan, D. Ostrander, U. Erb, G. Palumbo & K.T. Aust, *Scripta Metall. et Mater.*, **25**, 2711 (1991).
60. D. Osmola, P. Nolan, U. Erb, G. Palumbo & K.T. Aust, *Phys. Stat. Sol.*, **A131**, 569 (1992).
61. A.M. El-Sherik, K. Boylan, U. Erb, G. Palumbo & K.T. Aust, *Proc. Mat. Res. Soc. Symp.*, **238**, 727 (1992).
62. U. Klement, U. Erb & K.T. Aust, *Nanostructural Materials*, **6**, 581 (1995).
63. U. Klement, U. Erb, A.M. El-Sherik & K.T. Aust, *Mat. Sci. Eng.*, **A203**, 177 (1995).
64. N. Wang, Z. Wang, K.T. Aust & U. Erb, *Acta Mater.*, **45**, 1655 (1997).
65. G.D. Hibbard, K.T. Aust, G. Palumbo & U. Erb, *Scripta Mater.*, **44**, 513 (2001).
66. G.D. Hibbard, J.L. McCrea, G. Palumbo, K.T. Aust & U. Erb, *Scripta Mater.*, **47**, 83 (2002).
67. T.R. Haasz, K.T. Aust, G. Palumbo, A.M. El-Sherik & U. Erb, *Scripta Metall. et Mater.*, **32**, 423 (1995).
68. T. Turi, "Thermal and Thermodynamic Properties of Fully Dense Nanocrystalline Ni and Ni-Fe Alloys", Ph.D. Thesis, Queen's University, Kingston, Ontario, Canada, 1997.
69. T. Turi & U. Erb, *Mat. Sci. Eng.*, **A204**, 34 (1995).
70. A.M. El-Sherik, U. Erb, V. Krstic, B. Szpunar, M.J. Aus, G. Palumbo & K.T. Aust, *Proc. Mat. Res. Soc. Symp.*, **286**, 173 (1993).
71. V. Krstic, U. Erb & G. Palumbo, *Scripta Metall. et Mater.*, **29**, 1501 (1993).
72. U. Erb, G. Palumbo, B. Szpunar & K.T. Aust, *Nanostructural Materials*, **9**, 261 (1997).
73. R. Zugic, B. Szpunar, V. Krstic & U. Erb, *Phil. Mag.*, **A75**, 1041 (1997).
74. U. Erb, A.M. El-Sherik, G. Palumbo & K.T. Aust, *Nanostructural Materials*, **2**, 383 (1993).

75. M.J. Aus, B. Szpunar, U. Erb, G. Palumbo & K.T. Aust, *Proc. Mat. Res. Soc. Symp.*, **318**, 39 (1994).
76. B. Szpunar, U. Erb, K.T. Aust, G. Palumbo & L. Lewis, *Proc. Mat. Res. Soc. Symp.*, **318**, 477 (1994).
77. B. Szpunar, R. Zucic, U. Erb & L. Lewis, *Can. Met. Quarterly*, **349**, 281 (1995).
78. B. Szpunar, U. Erb, G. Palumbo, K.T. Aust & L.J. Lewis, *Phys. Rev. B*, **53**, 5547 (1996).
79. J. Weissmüller, R.D. McMichael, J. Barker, H.J. Brown, U. Erb & R.D. Shull, *Proc. Mat. Res. Soc. Symp.*, **457**, 231 (1997).
80. G. Palumbo, U. Erb & K.T. Aust, *Scripta Metall. et Mater.*, **24**, 2347 (1990).
81. A.H. Chokshi, A.H. Rosen, J. Karch & H. Gleiter, *Scripta Metall. et Mater.*, **23**, 1679 (1989).
82. G.W. Nieman, J.R. Weertman & R.W. Siegel, *Nanostructural Materials*, **1**, 185 (1992).
83. A.A. Karimpoor, U. Erb, K.T. Aust, Z. Wang & G. Palumbo, *Mat. Sci. For.*, **386-388**, 415 (2002).
84. R.B. Diegle & J.E. Slater, *Corrosion*, **32**, 155 (1976).
85. S.J. Thorpe, B. Ramaswami, & K.T. Aust, *J. Electrochem. Soc.*, **135**, 2162 (1988).
86. K. Hashimoto, K. Osada, T. Masumoto & S. Shimodaira, *Corrosion Sci.*, **16**, 71 (1976).
87. M. Naka, K. Hashimoto & T. Masumoto, *Corrosion*, **36**, 679 (1980).
88. P. Bragagnolo, Y. Waseda, G. Palumbo & K.T. Aust, *MRS Int. Mtg. Adv. Mat.*, **4**, 469 (1989).
89. R. Rofagha, S.J. Splinter, U. Erb & S.N. McIntyre, *Nanostructural Materials*, **4**, 69 (1994).
90. G. Palumbo, "Intergranular Corrosion in High Purity Nickel", Ph.D. Thesis, University of Toronto, Toronto, Ontario, Canada, 1989.
91. S. Wang, "Electrochemical Properties of Nanocrystalline Nickel and Nickel-Molybdenum Alloys", Ph.D. Thesis, Queen's University, Kingston, Ontario, Canada, 1997.
92. A. Alfantazi & U. Erb, *Corrosion*, **52**, 880 (1996).
93. S.H. Kim, K.T. Aust, U. Erb, F. Gonzalez & G. Palumbo, *Scripta Mat.*, submitted for publication (2002).
94. G. Hibbard, U. Erb, K.T. Aust, U. Klement & G. Palumbo, *Mat. Sci. For.*, **386-388**, 387 (2002).
95. A.V. Galina, V.Y. Fradkov & L.V. Shvindlerman, *Phys. Met. Metalloved.*, **63**, 1220 (1987).
96. G. Palumbo & K.T. Aust, *Mat. Sci. Eng.*, **A113**, 139 (1989).
97. G. Palumbo, K.T. Aust in "Grain Growth in Polycrystalline Materials," H. Weiland, *et al.* (eds.) TMS, Warrendale, PA, 1998; p. 311.
98. H. Gleiter, *Progr. Mater. Sci.*, **33**, 224 (1989).
99. J.L. McCrea, Ph.D. Thesis, University of Toronto, Canada (2001).
100. G. Palumbo, U. Erb, J.L. McCrea, G.D. Hibbard, I. Brooks, F. Gonzalez & K. Panagiotopoulos, *Proc. AESF SUR/FIN 2002*, AESF, Orlando, FL, 2002; p. 204.
101. D.H. Jeong, F. Gonzalez, G. Palumbo, K. T. Aust & U. Erb, *Scripta mater.*, **44**, 493 (2001).
102. A. Zimmerman, G. Palumbo, K.T. Aust & U. Erb, *Mat. Sci. Eng.*, **A328**, 137 (2002).
103. U. Erb, K.T. Aust, G. Palumbo, J. McCrea, & F. Gonzalez, in "Processing and Fabrication of Advanced Materials IX", T. S. Srinivasan, *et al.* (eds.), ASM International, Materials Park, OH, 2001; p. 253.
104. G. Palumbo, P.C. Lichtenberger, F. Gonzalez & A.M. Brennenstuhl, U.S. patents 5,527,445 (1996); 5,516,415 (1996); 5,538,615 (1996).
105. ASME Code Case 96-189-BC96-206 Case N-569; Section XI, Division 1; "Alternative Rules for Repair by Electrochemical Deposition of Class 1 and 2 Steam Generator Tubing," (1996).
106. G. Palumbo, P.J. King, K.T. Aust, U. Erb, & P.C. Lichtenberger, *Scripta Metall.*, **25**, 1775 (1991).
107. G. Palumbo, E.M. Lehockey, P. Lin, U. Erb, & K.T. Aust, *Proc. Mat. Res. Soc. Symp.*, **458**, 273 (1997).
108. H.K. Merchant, in "Defect Structure, Morphology and Properties of Deposits", H.D. Merchant (ed.), TMS, Warrendale, PA, 1995; p. 1.
109. U. Erb, K.T. Aust & G. Palumbo, in "Nanostructured Materials", C.C. Koch (ed.), Noyes Publ. /William Andrews Publ., Norwich, NY, 2002; p. 179.
110. J.L. McCrea, G. Palumbo, F. Gonzalez, A. Robertson, K. Panagiotopoulos, & U. Erb, *Proc. AESF SUR/FIN® 2001*, AESF, Orlando, FL, 2001; p. 149.

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