TOPICAL REVIEW

Electrodeposition of nanostructured coatings and their characterization—a review

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Received 10 October 2007
Accepted for publication 31 March 2008
Published 17 October 2008
Online at stacks.iop.org/STAM/9/043001

Abstract
Nanostructured materials have gained importance in recent years due to their significantly enhanced properties. In particular, electrochemistry has a special role in producing a variety of nanostructured materials. In the current review, we discuss the superiority of electrochemical deposition techniques in synthesizing various nanomaterials that exhibit improved characteristics compared with materials produced by conventional techniques, as well as their classification, synthesis routes, properties and applications. The superior properties of a nanostructured nickel coating produced by electrochemical deposition are outlined. The properties of various nanostructured coating materials produced by electrochemical techniques are also described. Finally, the importance of nanostructured coatings in industrial applications as well as their potential in future technologies is emphasized.

Keywords: nanostructured coatings, electrochemical deposition, characterization, applications

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Metallurgists and material scientists have been conducting investigations for the past several years to develop new materials with enhanced properties. Several new and nonequilibrium (metastable state) processing methods have been developed during the last few decades to improve the performance of existing materials. A novel method of transforming a material to a metastable state is to reduce its grain size to a few nanometers, at which the proportion of atoms in the grain boundaries is equivalent to or higher than those inside the grains. Materials with such small grain sizes are now referred to as nanocrystalline (NC) materials (and also as nanocrystals, nanostructures, nanophase materials or nanometer-sized crystalline solids), and have been shown to have much improved properties compared with those exhibited by conventional-grain-sized (>10 \(\mu\text{m}\)) polycrystalline materials. The combination of unique compositions and novel microstructures leads to the extraordinary potential of NC materials for a variety of structural and nonstructural applications.

Nanostructured coatings offer great potential for various applications due to their superior characteristics that are not typically found in conventional coatings. Because of the novel properties and various potential applications, NC materials, with typical grain sizes < 10 nm, are attracting increasing attention from researchers all over the world. Because of the small grain size of these materials and consequently the large volume fraction of atoms in or near the grain boundaries, these materials exhibit properties that are often superior and sometimes completely new, in comparison with those of conventional coarse-grained materials. These
Table 1. Classification of nanocrystalline materials.

| Dimensionality | Designation        | Typical method(s) of synthesis          |
|----------------|--------------------|----------------------------------------|
| Zero dimensional | Clusters           | Sol–gel method                         |
| One dimensional | Layered (lamellar) | Electrodeposition                      |
| Two dimensional | Filamentary        | Vapour deposition                      |
| Three dimensional | Crystallites       | Chemical vapour deposition              |
|                 | (equiaxed)         | Gas condensation                       |
|                 |                    | Mechanical alloying                    |

include increased strength/hardness, improved ductility/toughness, reduced density, reduced elastic modulus, higher electrical resistivity, increased specific heat, higher coefficient of thermal expansion, lower thermal conductivity, increased corrosion and wear resistance and superior soft magnetic properties. However, a full understanding of the structures, thermal stability and properties of these novel materials has not yet been achieved. A number of issues and properties are still to be addressed.

2. Classification

NC materials are single-phase or multiphase polycrystals, the crystal size of which is of the order of a few (typically 1–100) nanometers in at least one dimension. Thus, they can be equiaxed and are termed nanostructure crystallites (three-dimensional (3D) nanostructures), or they can have a lamellar structure and are termed layered nanostructures (two-dimensional (2D) nanostructures), or they can be filamentary (one-dimensional (1D) nanostructures). Additionally, zero-dimensional (0D) atom clusters and cluster assemblies are considered. Table 1 summarizes this classification and figure 1 illustrates the four types of nanostructures schematically. The length and width are much greater than the thickness in layered nanocrystals, and the length is substantially larger than the width or diameter in filamentary nanocrystals. NC materials may contain crystalline, quasi-crystalline or amorphous phases and can be metals, ceramics or composites.

Among the above materials, most attention has been paid to the synthesis, consolidation and characterisation of the 3D nanostructured crystallites followed by those of 2D layered nanostructures. While the former are expected to be used in applications based on their high strength, improved formability and soft-magnetic properties, the latter are intended for electronic applications. Relatively few investigations have been carried out on the 0D clusters and 1D filamentary nanostructures.

3. Synthesis

In principle, any method capable of producing polycrystalline materials with very fine grains can be used to produce NC materials. If a phase transformation is involved, e.g. liquid to solid or vapor to solid, then steps have to be taken to increase the nucleation rate and decrease the growth rate during the formation of the product phase. NC materials can be synthesized by a number of techniques with the starting material existing either in the vapor, liquid or solid state. Inert gas condensation, in which the evaporated material is quenched onto a cold substrate, was the first technique used to synthesize NC metals and alloys. Subsequently, plasma processing and physical and chemical vapor deposition have also been used. Electrodeposition (ED) and rapid solidification processing use the liquid state as the starting material. Mechanical alloying, friction stir welding, severe plastic deformation, spark erosion, sliding wear and repeated cold rolling produce NC materials in the solid state. While some of these techniques are in commercially use for large-scale production (e.g. inert gas condensation, ED and mechanical alloying), many other techniques are essentially used only for laboratory investigations. Most of the early studies (1975–1990) dealt with materials produced by the crystallization of amorphous precursor materials. The second group of materials that have been extensively studied since 1990 are nanostructures produced by ED. Table 2 shows the major improved properties of typical NC nickel produced by ED [1–16].

Nanostructured materials often exhibit outstanding properties compared with those of bulk materials as mentioned earlier. Therefore, these materials have become extensively used worldwide in a variety of applications. ED is a unique technique in which a variety of materials can be processed including metals, ceramics and polymers. Electrochemical strategies offer important advantages and
Table 2. Improved properties of nanocrystalline nickel.

| Property            | Observation                              | References |
|---------------------|------------------------------------------|------------|
| Hardness            | 5 times harder                           | [1–4]      |
| Friction            | Reduction in coefficient of friction by 50% | [5]        |
| Corrosion resistance | Improved significantly                   | [6–8]      |
| Strength            | 3 to 10 times stronger                   | [9]        |
| Wear resistance     | Increased by a factor of 170             | [5]        |
| Magnetic            | Lower coercivity, increased resistivity by a factor of 3 times, Ms reduced by 5% | [10–13]    |
| Hydrogen diffusion  | Higher hydrogen diffusion                 | [14–15]    |
| Electro catalytic    | Improved electrocatalytic activities for hydrogen evolution and hydrogen oxidation reactions | [16]       |

Figure 2. General schematic diagram for electrodeposition process.

unique possibilities in the development of nanomaterials and nanostructures. Recently, novel ED technologies have evolved into an important branch of nanotechnology. Using this technique, it is possible to obtain pore-free NC metal specimens in a single step process [17, 18]. To gain a better understanding of the nature of the crystalline state, it may be useful to establish the similarities and differences in the microstructures of NC metals manufactured via different technological routes. It was reported that the microstructures of NC Ni and Cu obtained through ED and severe plastic deformation (SPD) techniques are different. For ED Ni, the grain structure is controlled by the parameters of the layer growth process and by the misfit between the crystal structures of the deposit and substrate. On the other hand, the structure of SPD Ni is controlled by the movement of dislocations created by the applied deformation [19].

The co-deposition of ceramic materials with metals and polymers has created opportunities for the preparation of novel hybrid nanomaterials and nanostructures that cannot be obtained by other methods. Figure 2 shows a general schematic diagram of the ED process. To obtain enhanced characteristics of any nanocoating, it is essential to optimize the bath (electrolyte) composition as well as the deposition parameters in addition to selecting appropriate anode and cathode materials with a suitable coating. For example, table 3 shows the bath composition as well as the deposition parameters for producing Ni–AlN nanocomposite coatings. Similarly, optimized parameters and bath composition are paramount in the ED of any new coating or material. Recent research has been focused on demonstrating the feasibility of co-depositing various nanomaterials and the development of novel electrochemical strategies. Nanohybrids have been combined resulting in advantageous properties compared with those of individual materials and exhibit novel and advanced properties not achievable in single phase materials.

The technique used for the synthesis of NC materials is determined by the ease of the process, its economic viability, its scalability and the desired purity of the end product. Most of the techniques referred to previously produce the NC material in the powder form. The application of NC materials requires that these powders are consolidated to their full density with minimal porosity, and this is not easy to achieve. Full densification with complete interparticle bonding requires the exposure of the powder to high temperatures and pressures for extended periods of time, which is likely to coarsen the microstructural features. The retention of the material in the NC state, however, warrants that the powder is not exposed to high temperatures for longer periods of time; this may not result in complete densification. Thus, successful consolidation to full density requires innovative methods of consolidation. However, since NC materials have a large fraction of the atoms in the grain boundaries, the diffusivity of NC materials is much higher than that of a coarse-grained material of same composition. This allows the full consolidation of NC materials at temperatures 300 to 400 °C lower than those required for the coarse-grained materials. The successful consolidation of NC
powders has been achieved by electrodischarge compaction, plasma-activated sintering, shock consolidation, hot isostatic pressing (HIP), ceracon processing, hydrostatic extrusion, strained powder rolling and sinter forging [20]. Consolidation is not required if the powder can be used as it is (e.g. in slurries, as catalysts or for coating purposes). It is critical to synthesize nanosized powders in a clean environment, and powders that are susceptible to contamination by oxygen and moisture must be protected during storage and transport. However, the nanostructured materials produced by ED and amorphous crystallization that lead to the direct fabrication of high-density bulk materials are not subject to these concerns.

4. Specific advantages of electrochemical deposition

The synthesis of nanomaterials requires an atomistic deposition process and extreme control over the deposition. Vapor deposition techniques have been used almost exclusively to produce these materials. The fact that electrochemical deposition, also being an atomic deposition process, can be used to synthesize nanocomposites, has generated a great deal of interest in recent years. The obvious advantages of this century-old process of ED are as follows:

a. Rapidity
b. Low cost
c. Free from porosity
d. High purity
e. Industrial applicability
f. Potential to overcome shape limitations or allows the production of free-standing parts with complex shapes
g. Higher deposition rates
h. Produce coatings on widely differing substrates
i. Ability to produce structural features with sizes ranging from nm to µm
j. Easy to control alloy composition
k. Ability to produce compositions unattainable by other techniques
l. The possibility of forming of simple low-cost multilayers in many different systems, e.g. Cu/Ni, Ni/Ni–P etc.
m. No postdeposition treatment

The formation of nuclei on an electrode substrate was extensively studied on the basis of macroscopic thermodynamic considerations. The nucleation of nanostructures on the electrode substrate during ED is affected by the crystal structure of the substrate, specific free surface energy, adhesion energy, lattice orientation of the electrode surface and crystallographic lattice mismatch at the nucleus-substrate interface. The final size distribution of the electrodeposited material, however, strongly depends on the kinetics of the nucleation and growth. The ED process involves either instantaneous or progressive nucleation. In the case of instantaneous nucleation, all the nuclei form instantaneously on the electrode substrate and subsequently grow with increasing time of ED. In contrast, the number of nuclei that form is a function of the time of ED in
progressive nucleation. These nuclei gradually grow and overlap; therefore, progressive nucleation produces zones of reduced nucleation rate around the growing stable nuclei.

The ED technique consists of an electrochemical cell and accessories for applying a controlled current at a certain voltage. The cell usually contains a reference electrode, a specially designed cathode and an anode or counter electrode. The cathode substrate on which ED of the nanostructure takes place can be made of either nonmetallic or metallic material. Using the surface of the cathode as a template, various desired nanostructures or morphologies can be synthesized for specific applications. Such a template-assisted ED process can be broadly divided into two types: active template-assisted and restrictive template-based ED.

The formation of nanostructures in assisted synthesis results from the growth of nuclei that invariably nucleate the holes and defects of the electrode substrate. The subsequent growth of these nuclei at the template yields the desired surface morphology of the nanostructures, which can therefore be synthesized by choosing an electrode with an appropriate surface. Highly oriented pyrolitic graphite (HOPG), for example, is used extensively as an electrode substrate for the ED of silver, gold, molybdenum, palladium and platinum nanostructures. ED initiates at the step edges, dislocations and defect sites of the electrode surface.

Another method of template-assisted synthesis of mainly used for the growth of metal nanowires involves the
deposition of metal into the cylindrical pores or channels of an inert, nonconductive nanoporous electrode material. Track-etch membranes, porous alumina and other nanoporous structures including conductive rubber polymers, metals, semiconductors, carbons and other solid materials have been used as templates to prepare nanometer-sized particles, fibrils, rods and tubes.

Although a variety of templates and ED processes have been reported in the literature, reports on the universal application of such templates for depositing metallic nanostructures with controlled and well-defined morphologies are lacking. The major problem with using ED to synthesize nanostructures is the preparation of suitable templates. ED is strongly affected by the surface characteristics of the electrode substrate, and the shape and size of the deposit depend on the substrate. Therefore, further studies on electrode surfaces and subsequent surface engineering are essential to develop active templates for the successful synthesis of nanostructures using ED.

A number of advances have recently contributed to the use of ED for the fabrication of nanostructured ceramic materials, and considerable attention has been given to the electrochemical deposition of ceramic coatings for biomedical applications. For such applications, thin films of hydroxyapatite (HAP) were prepared using an ED technique (electrophoretic deposition (EPD) [21, 22] or electrolytic deposition (ELD) [23]. HAP is an established implant material because its chemical composition is similar to that of bone tissue. ED was utilized for the preparation of coatings on Ti-6Al-4 V surgical alloy substrates. In this process, the prepared coatings exhibited enhanced sinterability at relatively low temperatures. Nanostructured coatings of HAP were also prepared by ED from aqueous solutions containing calcium and phosphate ions. The electrochemical method is a novel approach to the synthesis of biomedical coatings and composites. Moreover, it provides an important contribution to the development of nanostructured compounds. Nanostructured ZnO obtained from ED has important applications in chemical sensors, semiconductor diodes, catalysis and solar cells [24–26]. Electrodeposited titania is used in gas sensors, solar cells, biomedical implant, and electrochromic devices. Varying the bath compositions and deposition parameters allows control over the morphology and porosity of the films. The nanostructured films have important advantages for applications in solar cells. The possibility of defect chemistry superlattices modulated on a nanometer scale is another exciting development. The fabrication of ceramic nanowires by ED is another area of interest.

Cathodic ED enables the formation of ceramic particles in situ in a polymer matrix, preventing particle agglomeration. An important development in this area is the ED of hybrid films based on Fe$_2$O$_3$ and poly-diallyltrimethylammonium chloride (PDDA). It was reported that the hybrid films had superparamagnetic properties at room temperature. Hybrid polymer-ceramic films can be prepared on cathodic and anodic substrates by the co-deposition of ceramic nanoparticles and polymers or by the electrochemical intercalation of ceramic particles into the polymer matrix at the electrode surface. Various electrochemical techniques have been developed for the preparation of nanostructured hybrid metal/metal-oxide materials [27–30].

Ni–P deposits obtained from ED are important materials for the surface finishing of industrial materials owing to their electrocatalytic activity for hydrogen evolution, special paramagnetic properties, excellent microhardness and corrosion resistance [31, 32]. Electrodeposited amorphous Ni–P alloys possess a more regular amorphous structure and lower concentration of defects than melt-spun Ni–P alloys [33, 34].

It was reported that nanocomposite layers can be obtained by the electrochemical deposition of silicon carbide nanoparticles (mean diameter 20 nm) in a nickel-plating bath. Benea et al [35] showed that the incorporation of 20 nm SiC particles during Ni deposition modifies the impedance and cathodic polarization due to the modification

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**Figure 8.** Microhardness as a function of wt.% SiC in nanocomposite Ni–SiC coatings (reprinted from [73], © 2002, with permission from Elsevier).

**Figure 9.** Relationship between hardness and Taber wear resistance of nanocrystalline Ni and Ni–P coatings (reprinted from [74], © 2003, with permission from Elsevier).
of the surface morphology and crystallinity of the nickel matrix. Spinvalve-type multilayered structures in the form of nanowires were deposited by Fedosyuk et al. [36] by pulsed ELD using a single electrolyte.

Among the diverse synthesis processes, the electrochemical method has been used to synthesize a wide range of nanostructured materials, e.g. metal nanoparticles, nanowires, nanofilms, bulk NC metals, laminated composites, multilayered coatings and nanoparticle-reinforced composite coatings. TiO$_2$-nanoparticle-reinforced Ni composite coatings obtained by ED exhibit unusual photoelectrochemical characteristics, which can be used to study electronic transitions in semiconductors [37]. The cycle performance of a nanosized Cu$_6$S$_5$Ni electrode (used for secondary lithium batteries) prepared by chemical reduction is significantly enhanced in comparison with that of the same material prepared by sintering or mechanical alloying [38]. Gao et al. [39] synthesized Cu nanowires, which are dense, continuous and with uniform diameter (60 nm) along the entire length of each wire, by the potentiostatic electrochemical deposition of copper sulphate solution within the nanochannels of porous anodic alumina templates. Gorer et al. [40] showed that the use of ED for nucleation enables the instantaneous preparation of nanoparticles on graphite and silicon.

Silver nanorods were prepared by an electrochemical technique from an aqueous solution of AgNO$_3$ in the presence of polyethylene glycol (PEG), and it was found that the concentrations of AgNO$_3$ and PEG affect the formation of nanorods [41]. Electrochemically prepared Co nanofilms exhibit three to five times greater coercivity (H$_c$) than polycrystalline Co [42]. Fe nanowires were electrodeposited into the holes of porous anodic aluminium oxide (AAO), which was prepared electrochemically. Magnetic measurements showed that its easy magnetization direction is perpendicular to the sample plane. This type of nanowire array has potential applications in perpendicular magnetic recording [43]. The electrochemical reduction of metal oxides is an appropriate technique for the production of NC mesoporous metals at room temperature, which was demonstrated by producing Cu from polycrystalline sintered CuO and Cu$_2$O single crystals [44].

Some NC alloys exhibit excellent resistance to corrosion and can be used as protective coatings. One of the techniques for obtaining NC alloy coatings is by ED from aqueous solutions. The substrates coated with NC deposits such as Fe–Cr–P were found to increase their corrosion resistance significantly [45]. The voltammetric behavior of gold nanowire arrays prepared by the electrochemical method showed a significant enhancement of the ratio between the total electrolytically exposed surface area and the surface area accessible by diffusion in comparison with macroscopic flat gold electrodes [46]. Electrochemically deposited nanostructured platinum metals exhibit higher catalytic performance and stability for various catalytic reactions, as well as having unique magnetic properties, compared with conventional metals [47]. The synthesis of Co and Fe nanowires and nanotubes electrochemically deposited through nanoporous membranes was reported [48]. ED was reported to be an ideal technique for the preparation of high-performance Sn–Sb nanostructured electrode alloys used in lithium-ion batteries [49].

It is possible to measure the grain growth of NC silver by measuring the reversible electromotive force. The grain growth of the deposit can be quantitatively determined from the decrease in the electrode potential with time [50]. NC FeTi, LaNi$_5$, Mg$_2$Ni and other materials based on Mg were reported to easily absorb hydrogen at low temperatures with very good kinetics and are not sensitive to exposure to air [51]. Chen et al. [52] reported that the nanosize Ni particles with a Ce shell structure have superior hydrogen-storage properties due to the synergistic effect of Ce and Ni in the shell structure. Layered Cu-Ni nanocomposites prepared by ED showed enhanced hardness [53]. Nanocomposite Ni/Al$_2$O$_3$ film produced by ED, where 50 and 300 nm Al$_2$O$_3$
particles are dispersed in a Ni matrix, exhibit considerable enhancement in hardness in comparison with pure Ni [54].

Alternating layers of two different materials with different laminate thickness in the range of nanometers can be fabricated by electrochemical deposition. This technique demonstrates the capability of this relatively inexpensive process for the production of advanced materials with ultra fine microstructure [55]. NC nickel of about 17 nm size produced by ED significantly enhances the electrocatalytic activity for hydrogen evolution due to the increased density of active surface sites [56].

Electrodeposited Co–Ni–Cu/Cu superlattices showed a previously unreported transition from giant magnetoresistance (GMR) to anisotropic magnetoresistance (AMR) and back to GMR upon annealing. Transmission electron microscopy (TEM) investigations on Co–Ni–Cu/Cu superlattice nanowires revealed extensive twinning, while magnetotransport measurements confirmed that these superlattice nanowires exhibit CPP-GMR [57]. By suitably controlling the electrochemical deposition conditions, a wide range of artificially structured coatings such as epitaxial multilayered materials (Cu/Ni) and amorphous materials in combination with crystalline materials (NiPx/Sn) can be deposited [58]. Blondel et al and others [57, 59] have shown the possibility of measuring the CPP-GMR as a function of temperature for samples with resistance values reaching hundreds of ohms by fabricating multilayered nanowires by ED. Multilayered Co/Cu wires produced by ED with layer thickness in the range of 3 to 100 nm exhibited a GMR effect similar to that of sputtered samples [60].

Electrochemistry is a key technology in nanoparticle science. For example electroplating offers novel routes to nanosized particles via arrested and templated ED. Electrochemistry is a suitable method for coupling particle activity to external circuitry in nanoparticle science in fields such as optoelectronics and biological sensors. Electrochemistry is an enabling technology across the whole spectrum of nanoparticle research, from particle preparation to sensor applications and from band-gap determination to solar cell operation [61].

5. Structure

To understand the interrelationship between structure and properties, NC materials must be characterized on both atomic and nanometer scales. The microstructural features of importance include

(i) grain size, distribution and morphology,
(ii) the nature and morphology of grain boundaries and interface phases,
(iii) the nature and removal of intragrain defects,
(iv) composition profiles across grains and interfaces, and
(v) identification of residual species trapped during processing.
In the case of layered nanostructures, the features of importance are
(a) the thickness and coherency of interfaces,
(b) composition profiles across interfaces, and
(c) the nature of defects.

There is a wide range of characterization techniques that can yield structural information on NC materials. These include direct microscopic techniques such as TEM, scanning tunneling microscopy (STM), field ion microscopy (FIM), and the less direct electron, x-ray and neutron diffraction techniques. Indirect spectroscopic tools such as extended x-ray absorption fine structure (EXAFS), nuclear magnetic resonance (NMR), Raman and Mössbauer spectroscopy, and positron annihilation spectroscopy have also been used. Other useful tools employed include differential scanning calorimetry (DSC), mass spectroscopy, x-ray fluorescence, atomic absorption spectroscopy, Auger electron spectroscopy and hydrogen absorption.

Owing to the ultrafine scale of these materials, conventional characterization tools such as TEM and x-ray and neutron diffraction are both necessary and useful for determining the structure of NC materials. However, for microchemical analysis on the requisite fine scale, further advances in the capabilities of state-of-the-art instruments will be necessary to obtain the desired lateral scale resolution. Only atom probe FIM and STM offer the required lateral scale resolution for such chemical analysis at present.

The volume fraction of atoms residing in or near the grain boundaries increases as the grain size decreases. Consequently, in materials with a small grain size of a few nanometers, the fraction of atoms in the grain boundaries is comparable to that in the grains. Therefore, NC materials can be considered to consist of two structural components, i.e. small crystallites with long-range order and different crystallographic orientations constituting the crystalline component, and a network of intercrystalline regions (grain boundaries, triple junctions, etc), the structure of which differs from region to region, referred to as the interfacial component. A number of studies have been devoted to determining the structure of the crystallites and the interfaces using the above-mentioned techniques, and most of the results have been interpreted in terms of a two-component microstructure—a regular long-range ordered atomic arrangement in the grains and a random interfacial component. It has been speculated that the structure of the grain boundaries in NC materials might have unique characteristics owing to the constraints imposed on the grain boundary atoms by their synthesis via cluster consolidation. It has been noted that the structure of the crystallites is essentially the same as that of the coarse-grained materials, with the difference that the lattice parameters in the NC condition are slightly larger (0.2% to 0.8%) [63, 64]. The structure of the grain boundaries have been investigated in detail using high-resolution TEM techniques; the results are still inconclusive. There are two schools of thought regarding the grain boundary structures, one suggesting a gaslike disorder at the grain boundaries [65] and the other suggesting that the structure of the grain boundaries is the same in both NC and coarse-grained materials [66]. The latter suggestion has gained widespread acceptance in recent years [67]. However, further research is needed to better understand the structures of nanomaterials produced by different techniques.

6. Properties
Because of the very fine grain sizes, NC materials exhibit a variety of properties that are different and often considerably improved in comparison with those of conventional coarse-grained polycrystalline materials. These include morphological/structural properties (figures 3–5) [68–70], higher electrical resistivity (figure 6) [71], increased strength/hardness (figures 7–10) [1–4, 9, 72–75], enhanced diffusivity [9, 14, 15], improved ductility/toughness [3], reduced density, reduced elastic modulus, increased specific heat, higher thermal expansion coefficient, lower thermal conductivity [10–13], enhanced corrosion and wear resistance (figures 9, 11–12) [5–8, 72, 74], and superior reflectance (figure 13) [76] and soft-magnetic properties [10–13] in comparison with conventional coarse-grained materials. All these properties must be investigated extensively for new materials with a view to exploring possible applications in a variety of areas.

7. Industrial applications
As a result of the unique properties of electrodeposited nanomaterials, a number of industrial applications have emerged, some of which are presented in table 4. For example, the combination of increased hardness/wear resistance and reduced localized corrosion results in improved protective coating performance. Protective materials can be used as a hard surface on softer, less wear resistant substrates. For electroformed products such as printing mandrels and

| Table 4. Examples of electrodeposited nanomaterials and their potential applications. |
|---------------------------------|----------------------------------------------------------|
| Materials                      | Applications                                              |
| Pd, Ni–Pd                      | Hydrogen storage and purification, electrodes             |
| Ni – Al, Ni – SiC               | Corrosion protection, wear resistance                     |
| Co, Co – W, Co – P             | Hard coatings, magnetic materials                         |
| Ni, Ni – P, Ni – Mo, Ni – Zn, Ni – Fe, Ni – Fe – Cr | Corrosion protection, stress corrosion, soft magnets, catalysts |
CD stampers, a longer lifetime is expected. The magnetic and electrical properties make electrodeposited nanomaterials attractive as soft magnets for high-efficiency transformers, power supplies and motor applications. Next-generation recording head materials may also benefit from their excellent magnetic, electrical and wear properties. The exceptional catalytic properties make them strong contenders for different applications such as electrodes for hydrogen evolution and fuel cells. Some NC alloys exhibit very high hydrogen solubility, making them suitable candidates for hydrogen-storage materials. As a result of the enhanced properties of electrodeposited nanomaterials, a wide range of materials can be synthesized and used in a variety of applications to achieve enhanced efficiency. In essence, the effective commercialization of nanomaterials is expected to enhance the production of many materials by a factor of several times by significantly improving the efficiency of the fabricating systems.

A growing number of companies are aiming to scale up their production capabilities of nanostructured products and incorporate them into new and existing markets. In the United States alone, more than 70 companies are currently at various levels in the development and production of nanostructured materials. More than a dozen of these businesses are involved in the manufacture of nanostructured materials on an industrial scale. For example, among other products, nanosized particles are incorporated into commercially available abrasive polishing slurries, fire-retardant materials, magnetic fluids, magnetic recording tapes, sunscreens and transport systems. Bulk nanostructured materials such as soft-magnetic iron-based alloys are also in industrial use. By the end of this century, nanostructured materials are expected to play a significant role in many major industries.

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