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 manometers. 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 govemment-sponsored nanotechnology initiatives in many countries around the world. This paper reviews recent advances in the field of nanostructured materials produced by electrodeposition which, over the past decade, has evolved 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.

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1. Introduction

It is now generally accepted that “Nano”, the latest buzzword in science and technology, will form the basis for the next industrial revolution of the 21st century. 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. With the ever increasing resolving power of characterization techniques that are used to look at atoms and molecules (e.g. microscopy, spectroscopy, diffraction) over the past few decades and the development of new tools to actually pick up and manipulate individual atoms or molecules (e.g. atomic force microscopy) or very small objects (e.g. nanotweezers), this dream has now become reality. In the so-called bottom-up approach, nanostructures can now be created atom-by-atom or by assembly of components consisting of a few thousand atoms or molecules. Processes such as self organization, self assembly or templating can be used to build a multitude of small wonders including quantum computers with single electron memory, molecular motors, biosensors and endless other nanoarchitectures. While the large scale implementation of many of these futuristic applications is still several years or decades away, many people agree that this technology has a tremendous long term potential: to completely revolutionize society resulting, among other things, in a better understanding of nature, better quality of life and increased productivity.

One particular area of nanotechnology that is already much closer to reality deals with nanostructured materials in which the properties of materials used in relatively conventional products can be tremendously improved by grain or crystal size control. The main structural characteristic of these materials is the enhanced volume fraction of atoms located at the interfaces or grain boundaries between differently oriented grains. As shown in Fig. 1 [after ref. 1] for conventional polycrystalline materials with grain sizes larger than 1μm (10^3 nm) this volume fraction is much smaller than 1%. However, when the grain size is reduced to values less than 100 nm (which is usually considered to upper grain size limit for nanocrystalline materials) this volume fraction increases to significant values. For example, at 10 nm the volume fraction is about 30% and for grain sizes less than 5 nm the number of atoms associated with grain boundaries is actually higher than the number of atoms located in perfect crystal positions. It is therefore not surprising that nanocrystalline materials exhibit considerable changes in many of their physical, chemical and mechanical properties.

Over the past few years close to 200 different synthesis routes for the manufacture of nanocrystalline materials have been developed (e.g. refs. 2-6). Top-down approaches which use conventional bulk starting materials include solid state processing (e.g. mechanical attrition, severe plastic deformation, crystallization of amorphous precursors) and liquid phase processing (rapid solidification, atomization). Bottom-up methods produce materials, often under conditions far from equilibrium, in an atom-by-atom fashion such as in vapour phase processing (e.g. physical and chemical vapour deposition, inert gas condensation, sputtering), chemical synthesis (e.g. sol-gel, precipitation) and electrochemical synthesis (e.g. electroplating, electroless plating).

Many of these techniques produce nanostructured powders which must be further processed in secondary processing steps (e.g. hot isostatic pressing, sintering, thermal spraying) to produce useful materials.

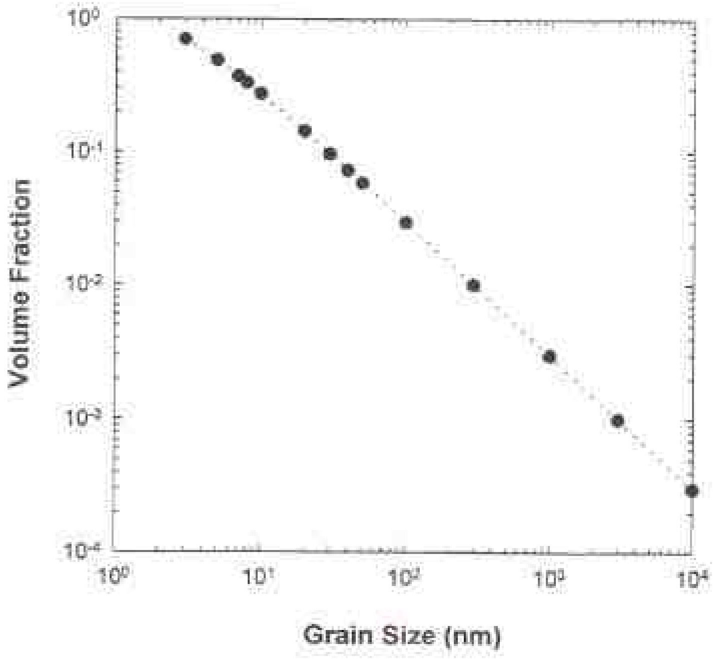


Figure 1. Effect of grain size on the volume fraction of atoms associated with the interface component (grain boundaries, triple junctions) assuming a grain boundary thickness of 1nm.

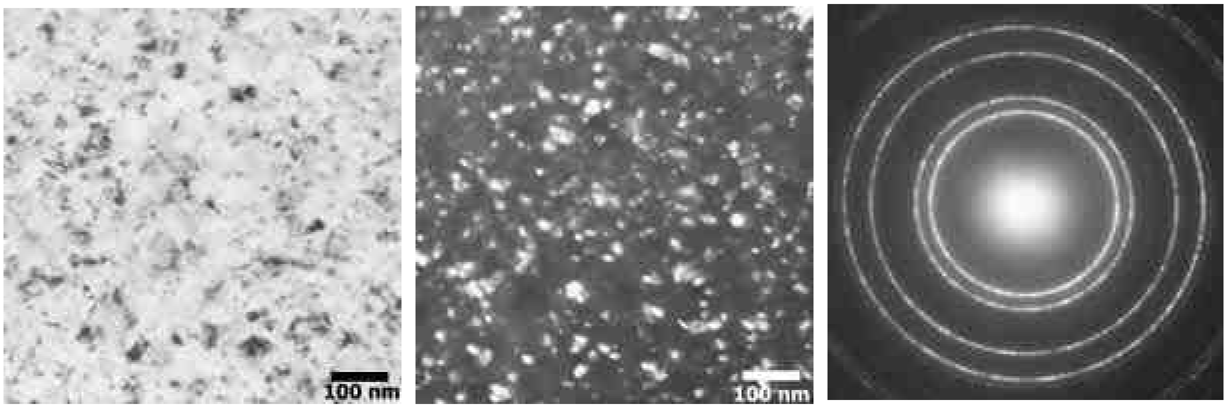


Figure 2. Transmission electron micrographs (brightfield, darkfield and diffraction pattern) of nanocrystalline nickel produced by pulse electrodeposition from a modified Watts baths.

This paper deals with nanocrystalline materials produced by electrodeposition, which is of considerable interest to electroplating industries. We first reported on electrodeposited nanostructures to this community at the AESF SUR/FIN conference in 1995 [7] and then again in 2001 [8-11] and 2002 [12-14]. Following the establishment of the AESF subcommittee on Nanostructured Materials at SUR/FIN 2002 in Chicago, a comprehensive review on nanostructured materials under the same title as the current paper was recently published in Plating and Surface Finishing [15]. Other relevant review articles on this topic can be found in references 16 to 19.

2. Synthesis and Structure of Electrodeposited Nanocrystals

Electrodeposition is a low-temperature processing route to produce nanostructured materials, most often in a single step requiring no secondary consolidation. Two electrodes are involved (one anode and one cathode) which are immersed in an aqueous electrolyte containing the material to be produced in ionic form. Important processing parameters include bath composition, pH, temperature, overpotential, bath additives, etc. Numerous examples listing electrochemical processing windows which lead to nanocrystal formation have been previously published for pure metals (e.g. Ni, Co, Pd ,Cu, Ag), binary alloys (e.g. Ni-P, Ni-Fe, Zn-Ni, Pd-Fe, Co-W) and ternary alloys (e.g. Ni-Fe-Cr, Ni-Fe-Co). Multilayered or compositionally modulated alloys (e.g. Cu-Pb, Cu-Ni, Ag-Pd, Ni-P), metal matrix composites (e.g. Ni-SiC, Ni-Al_2O_3, Co-WC, Co-B_4N), ceramics (e.g. ZrO_2) and ceramic nanocomposites (e.g. $Tl_a Pb_bO_c$) have also been successfully produced by electrodeposition methods [e.g. 15].

Electrocrystallization occurs either by the build up of existing crystals or the formation of new ones. These two processes are in competition with each other and are influenced by different factors such as plating parameters and substrate pre-treatment. The two key mechanisms which 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. The other important factor in nanocrystal formation during electrocrystallization is overpotential. Grain growth is favored at low overpotential and high surface diffusion rates for adions, while high overpotential and low diffusion rates promote the formation of new nuclei. In many systems these conditions can be achieved by using (1) pulse plating where the peak current density can be considerably higher than the limiting current density attained in the same electrolyte during direct current plating and / or (2) surface active bath additions or alloying elements which lower the surface diffusion of adions. Under these conditions, which lead to massive nucleation and reduced grain growth, the effect of the substrate on the resulting bulk electrodeposit becomes negligible. Fig. 2 shows an example of the microstructure of nanocrystalline nickel produced by pulsed current electrodeposition.

A thin coating (thickness up to ~100μm) electroplated onto on a substrate to modify specific surface properties is probably the most widely known application of electrodeposition technologies. However, it should be noted that there are several other processes (e.g. brush plating, electrowinning and electroforming) which can be used to produce nanocrystalline materials as thick coatings (several mm or cm thick) or in freestanding forms such as sheet, foil, tubes, wire, mesh, plate and foam. Several examples of product forms available through electrodeposition are shown in Fig. 3. Compared with other synthesis techniques to produce

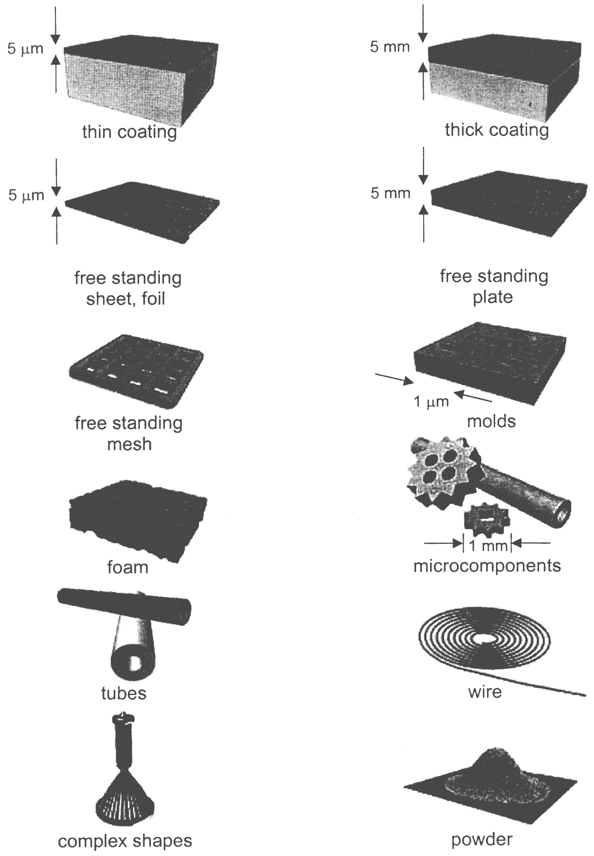


Figure 3. Examples of product forms for nanocrystalline materials produced by electrodeposition

- ☐ Offers the ability to synthesize a large number of metals, alloys, composite materials and compounds in various forms
- ☐ Production equipment requires only a modest capital investment
- ☐ Production rates are significant
- ☐ Flexibility with respect to product size, shape, grain size and particle size
- ☐ Flexibility to produce coatings, fully dense foils/plates and powders
- ☐ Commercial infrastructure for electroplating and electroforming already exists
- ☐ Only simple modification of bath chemistry and electrical parameters in conventional electroplating processes (bath/immersion-, barrel-, drum-, brush/selective-plating) are required
- ☐ The modified plating process can be used to produce fully-dense metals, alloys and metal matrix composites as free-standing forms or coatings as well as powders
- ☐ Proven technology, first commercial use was the Electrosleeve repair of nuclear steam generator tubes (1994)

Table 1. Electrodeposition offers several advantages over many other methods for nanocrystal synthesis.

nanocrystalline materials electroplating has many advantages as summarized in Table 1. Of greatest importance to the electroplating industry is the fact that nanostructured materials can be produced with existing infrastructure and require only minor modifications to currently available bath chemistries.

3. Properties of Nanocrystalline Electrodeposits

Early reports on the properties of nanocrystalline materials produced by vapour deposition methods showed many unexpected and often contradictory results (e.g. 19). It is now believed that some of these unusual results were mainly due to the limited quantities of materials available for property measurements as well as other defects such as porosity in materials produced by consolidation of precursor powders.

For fully dense nanocrystalline materials produced by electrodeposition with equiaxed grain size, log-normal grain size distribution and virtually zero porosity the effects of grain size (rather than porosity), and therefore interfacial volume fraction as per Fig. 1, can be readily assessed. Extensive measurements on such materials over the past decade have shown that some properties are strongly dependent on grain size, while for other properties crystal size has a negligible effect. Table 2 summarizes some of the findings for nanocrystalline Ni electrodeposits. Other nanocrystalline materials produced by electroplating show very similar property changes with grain size.

Nanocrystalline Ni electrodeposits show truly remarkable improvements in hardness, yield and tensile strength as well as wear resistance as seen from a comparison of data for conventional polycrystalline and nanocrystalline nickel with 100 nm and 10 nm grain sizes, respectively (Table 3). As for all metals, increasing strength and hardness in these materials comes at the expense of tensile ductility. However it should be noted that much higher ductility is found in bending or during rolling and other multiaxial deformation conditions. Fig. 4 shows that nanocrystalline Ni (15 nm grain size) can be deformed considerably by cold-swaging without any failure due to cracking and spalling.

Table 4 lists the Vickers hardness values for several nanocrystalline electrodeposits in the as-plated state. It should be noted that several of these metals exhibit hardness values comparable to hard chromium.

As a result of being non equilibrium structures in the as-plated state nanocrystalline electrodeposits can be produced as supersaturated solid solutions. Post plating annealing treatments of such alloys results in second phase precipitation making many alloys age hardenable as shown, for example, in the hardness as a function of annealing time curves for nanocrystalline Co-P alloys (Fig. 5). An additional benefit of second phase particle precipitation during annealing of such alloys is the thermal stabilization of the structure by pinning the grain boundaries. Through the so-called Zener pinning effect the temperature range for application of these materials can be increased considerably.

Strong Grain Size Dependence	**Negligible Grain Size Effects**
Hardness↑ Yield Strength↑ Tensile Strength↑ Tensile Elongation↓ Wear Resistance↑ Coefficient of Function↓ Electrical Resistivity↑ Magnetic Coercivity↑↓ Thermal Stability↓ Hydrogen Solubility↑ Solid Solubility↑ Localized Corrosion↓	Modulus of Elasticity Thermal Expansion Heat Capacity Magnetic Saturation Magnetization Resistance to Salt Spray Environment Thickness of Passive Layer

Table 2. Summary of properties of nanocrystalline nickel electrodeposits exhibiting strong and negligible grain size dependence.

Property	**Conventional †**	**Nano-Ni 100nm**	**Nano-Ni 10nm**
Yield Strength, MPa (25°C)	103	690	>900
Yield Strength, MPa (350°C)	–	620	–
Ultimate Tensile Strength, MPa (25°C)	403	1100	>2000
Ultimate Tensile Strength, MPa (350°C)	–	760	–
Tensile Elongation, % (25°C)	50	>15	1
Elongation in Bending, % (25°C)	–	>40	–
Modulus of Elasticity, GPa (25°C)	207	214	204
Vickers Hardness kg/mm^2	140	300	650
Work Hardening Coefficient	0.4	0.15	–
Fatigue Strength, MPa (10^8 cycles/air/ 25°C)	241	275	–
Wear Rate (dry air pin on disc), µm^3/µm	1330	–	7.9
Coefficient of Frictionality (dry air pin on disc)	0.9	–	0.5

† ASM Metals Handbook, ASM International, Metals Park, OH. Vol. 2, p. 437 (1993)

Table 3. Property comparison for conventional and nanocrystalline nickel.

Figure 4. Plain carbon steel pipe having a 0.010 in. OD coating of nanocrystalline Ni (15nm grain size) which has been cold-swaged (rotary) from a 2.5 in. to 2.0 in. diameter in a single step.

Chemical Composition	Average Grain Size, nm	Vickers Hardness No.
Nickel	11	660
Nickel - 7wt.% Molybdenum	14	620
Nickel – 0.5wt.% Phosphorus	<5	>1100
Nickel-20wt.% Iron	15	690
Nickel-15wt.%Chromium-10wt.%Iron	12	890
Cobalt	13	650
Iron	15	875
Iron – 40wt%Cobalt	15	750
Cobalt-12wt.% Tungsten	<100	550
Zinc-13wt.%Nickel	60	425
Zinc – 20wt% Nickel	<100	540

Table 4. Vickers hardness for various nanocrystalline metals and alloys in the as-plated condition.

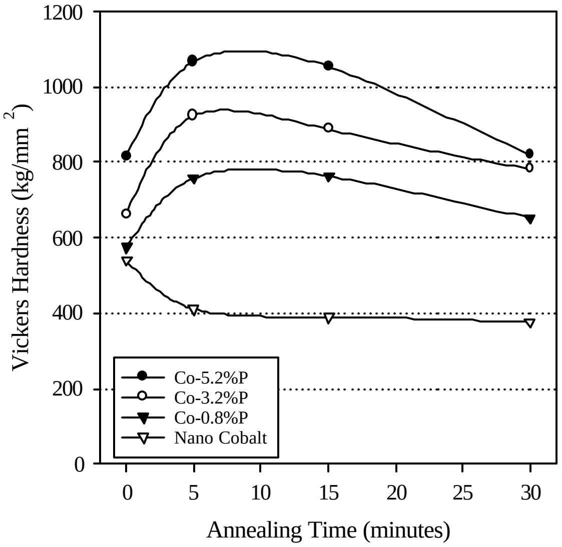


Figure 5. Age-hardenable nanocrystalline Co-P alloys

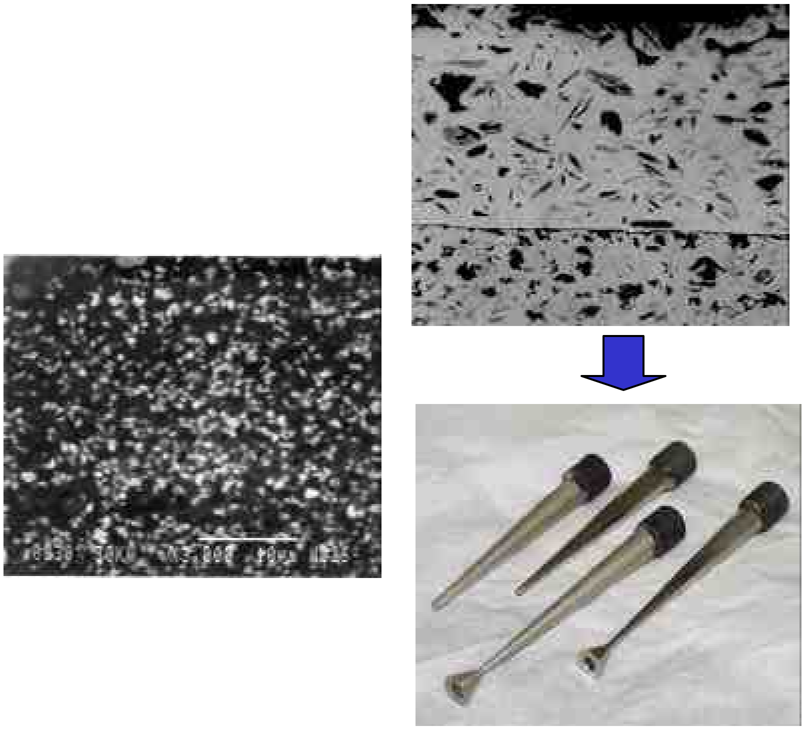


Figure 6. Application of nanocomposite coatings. Nano Co + WC (left) for hardfacing applications; Nano Ni + MoS_2 (right) as self-lubricating coatings on hydraulic expansion mandrels.

4. Applications

On the basis of well understood properties as a function of grain size, the industrial application of fully dense nanocrystalline materials has advanced rapidly in many different areas including wear and corrosion resistant coatings (e.g. as Cr or Cd replacement coatings), structural repair technology, soft magnetic materials, catalysts, copper foil for printed circuit board applications, high performance sporting goods and microelectromechanical systems (MEMS). Some of these will be discussed in the following sections.

4.1 Structural Repair

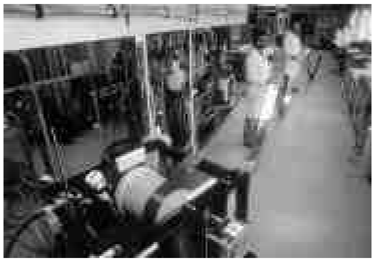
In this first large scale application of nanocrystalline materials which has been implemented in both Canadian CANDU and US Pressurized Water Reactors a nanocrystalline Ni-microalloy was electroformed in-situ as a thick (0.5-1.0 mm) coating on the inside surface of steam generator tubing to affect a complete structural repair to sites where the structural integrity of tubes had been compromised by corrosion and stress corrosion cracking. Details on this and other structural repair applications for nanocrystalline materials will be presented in the paper by Gonzalez et al. in this session.

4.2 Corrosion and Wear Resistant Coatings

Aerospace, automotive and defense industries have continuing need for high performance corrosion and wear resistant coatings in particular for non line-of-sight applications. The material requirements for such applications also include low porosity, excellent adhesion to the substrate and low coefficient of friction. Traditionally hard chrome and cadmium electrodeposits have been used for many applications. However in more recent years, as a result of the health risks and environmental concerns associated with these coatings there is considerable pressure to develop more benign replacement coatings. As shown in ref. 15, Co based nanostructured alloys and composite coatings can be produced by electrodeposition which meet or exceed the wear resistance of hard chromium. In the development of these coatings it was shown that high hardness is not the only requirement for excellent wear performance of a material. In addition to hardness factors such as ductility and the ratio of surface hardness to elastic properties also play important roles. This will be addressed in more detail in the paper by D. H. Jeong et al. in this session.

As will be discussed in the paper by Kim et al., grain size reduction in nanocrystalline materials results in considerable improvements in their resistance to localized corrosion such as pitting, intergranular attack and intergranular stress corrosion cracking thus reducing the probability of components to fail catastrophically. The relatively uniform corrosion observed in these materials is also of great importance in lifetime assessment considerations of component for specific industrial applications.

The incorporation of second phase particles by co-deposition offers the opportunity to tailor specific functional properties. Two examples of such coatings are shown in Fig. 6: Nano Co - WC for hard facing applications and nano Ni-MoS_2 for self-lubricating surfaces.



Electrodeposited nanocrystalline materials are a cost-effective, high performance alternative to commercial melt spun based magnetic products **[Finemet® (Hitachi); Vitrovac® & Vitroperm® (Vacuumschmelze); Metglas® (Honeywell)].**

Other Advantages:

Can be produced in a wide range of thickness (10μm-150μm) & width (up to 60cm), or electroformed to complex shapes.

Good ductility for easy core winding, assembly and handling.

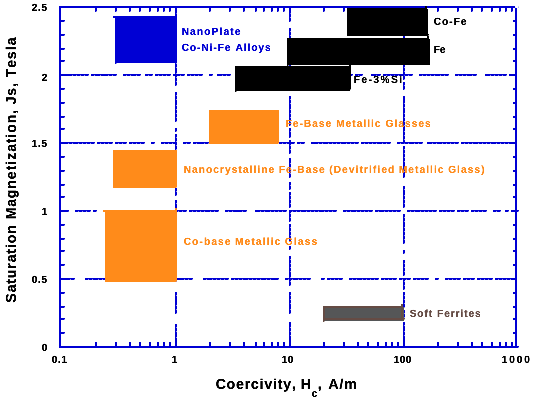


Figure 7. Synthesis of soft-magnetic sheet and foil.

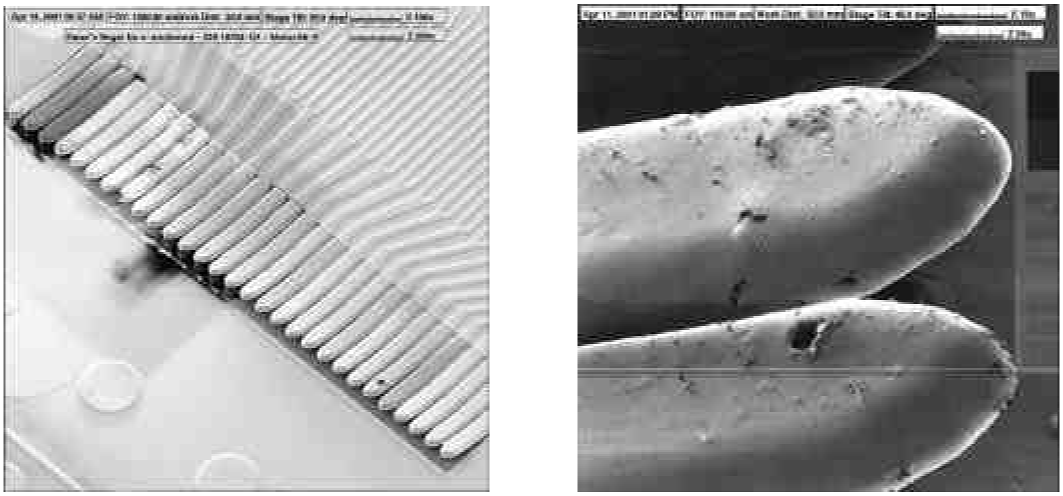


Figure 8. Nanocrystalline Ni-Mo microsprings.

4.3 Soft Magnets

Soft magnets for a wide range of applications (e.g. electromagnetic shielding, transformer core materials, high efficiency motors, magnetic recording heads) require primarily high permeability, saturation magnetization and electrical resistivity as well as low coercivity and magnetocrystalline anisotropy. High strength is also of importance in particular for thin foils and wires as is high corrosion and wear resistance when these materials are used as coatings. The main advantage of electrodeposited nanocrystals (compared to nanocrystals prepared from rapidly solidified amorphous materials or precursors powders) is their uncompromised saturation magnetization as the grain size is decreased to less than 100 nm. Electrical resistivity and coercivity requirements dictate that materials with grain sizes less than 20 nm should be used. The best combination of high saturation magnetization and low coercivity is expected for electrodeposited Co-Ni-Fe Nanoplate alloys as shown in Fig. 7 in comparison to currently available Fe and Co based metallic glasses and nanocrystalline Fe-based alloys produced by devitrification of metallic glass. Electrodeposition technology can readily implement the production of magnetic materials in a wide range of shapes (thin and thick coatings, continuous foil, wire, complex shapes.)

4.4 Microelectromechanical Systems

Microelectromechanical systems (MEMS) can be described as machines constructed of small moving and stationary components that have characteristic dimensions ranging from about 0.001 mm to 1 mm. The motivation for the development of such devices is the possibility of extending the advantages of small scale previously only available in electronic devices to fully functional mechanical systems on a scale that allows their integration in a single silicon chip or similar device. Over the past decade such devices have been developed for applications in many areas including biomedical, telecommunications, automotive, space exploration and consumer products. Many of these devices are Si based and several micromachining techniques have been developed to shape relatively complex structures out of single crystal starting materials. For metallic MEMS components through-mask electrodeposition has become the method of choice. This process is called LIGA which stands for Lithographie (lithography), Galvanoformung (electroforming) and Abformung (molding), originally developed in Germany. Examples of electroplated LIGA components include Ni and Ni-Fe microgears, Ni-nozzles for inkjet printers, Au microelectrodes for monitoring on chip fluid chemistry and Cu or Ag microcoils for microinductors and microelectromagnets. However in reducing the size of these devices several unexpected scaling effects were observed which have resulted in severe reliability issues in many of these microcomponents. One of the major problems in this respect is that electrodeposition of the metallic component is usually carried out under conditions which result in microstructures that are incompatible with the external size of the component. Most LIGA components show relatively large grained electrodeposits, very often with columnar structure. As a result, the overall strength of the component which contains only a few grains in cross section is very low, with the direct consequence that the component fails at relative low stress levels. Furthermore, since the elastic properties of most metals are dependent on the crystal orientation small variations in the crystallographic texture can result in large batch-to-batch variations in the spring constants of these materials.

These limitations of current LIGA products can be overcome by using plating conditions which result in nanocrystalline electrodeposits. By reducing the grain size of the components to levels many times smaller than the external dimensions the presence of hundreds or even thousands of small crystals in cross section will maintain the required high strength levels. Moreover, random crystal orientation ensures uniform elastic properties of the component eliminating the variations in the spring constants observed in conventional LIGA components. As an added benefit, the total elastic energy that can be stored in such a component (resilience) can be orders of magnitude higher than in conventional LIGA components. Resilience is given by s_y^2 / E, where s_y is the yield strength and E is the Young's modulus. With s_y for nanocrystalline being 5-10 times higher than for polycrystals and E being relatively independent of grain size, enhancements in resilience of up to 100 times over conventional LIGA components can be achieved. An example of a MEMS microcomponent is shown in Fig. 8. In this application uniform elastic response of the nanofingers was achieved by using a nanocrystalline Ni-Mo electrodeposit.

5. Conclusions

Many commercialization efforts for the mass production of nanocrystalline metals, alloys and composite materials using different synthesis routes are currently underway. Of all the techniques developed so far electrodeposition has been shown to be a technologically feasible and economically viable approach to produce materials with unique physical, chemical and mechanical properties. Consequently considerable opportunities exist for the electroplating industry to play a leading role in the development of superior nanomaterials for immediate application in many traditional areas. In addition, new markets and business opportunities are expected to emerge for this industry in the next several years; however nanomaterials will require novel but economic manufacturing technologies for mass production on a rapidly decreasing size scale.

References:

1) G. Palumbo, S. J. Thorpe and K. T. Aust, Scripta Metall. et Mater., 24 (1990) 1347
2) H. Gleiter, Nanostr. Mat., 1 (1992) 1
3) Proceedings of 2nd International Conference on Nanostructured Materials, H. E Schaefer et al., (eds.), Nanostr. Mat., 6 (1995) 1-1026
4) Proceedings of 3rd International Conference of Nanostructured Materials, M. L. Trudeau et al., (eds.), Nanostr. Mat., 9 (1997) 1-771
5) Proceedings of 4th International Conference on Nanostructured Materials, M. Muhammed and K. V. Rao (eds.), Nanostr. Mat. 12 (1999) 1-1188
6) Proceedings of 5th International Conference on Nanostructured Materials, A. Inoue et al., (eds.), Scripta Mater. 44 (2001) 1161-2372
7) R. Rofagha, D. Wood and U. Erb, AESF SUR/FIN '95 Technical Proc., AESF, Orlando, FL. (1995) 197

8) U. Erb, I. Brooks and A. Alfantazi, AESF SUR/FIN 2001 Technical Proc., AESF, Orlando, FL. (2001), CD-ROM section D
9) D. H. Jeong, U. Erb, K. T. Aust, A. Robertson, J. L. McCrea and G. Palumbo, AESF SUR/FIN 2001 Technical Proc., AESF, Orlando, FL. (2001), CD-ROM section D
10) S. H. Kim, F. Gonzalez, K. Panagiotopoulos, G. Palumbo, U. Erb and K. T. Aust, AESF SUR/FIN 2001 Technical Proc., AESF, Orlando, FL. (2001), CD-ROM section D
11) J. L. McCrea, G. Palumbo, F. Gonzalez, A. Robertson, K. Panagiotopoulos and U. Erb, AESF SUR/FIN 2001 Technical Proc., AESF, Orlando, FL. (2001), CD-ROM section D
12) D. H. Jeong, U. Erb, K. T. Aust and G. Palumbo, AESF SUR/FIN 2002 Technical Proc., AESF, Orlando, FL. (2002) 235
13) S. H. Kim, K. T. Aust, U. Erb, G. Ogundale and F. Gonzalez, AESF SUR/FIN 2002 Technical Proc., AESF, Orlando, FL. (2002) 225
14) G. Palumbo, U. Erb, J. L. McCrea, G. D. Hibbard, I. Brooks and F. Gonzalez, AESF SUR/FIN 2002 Technical Proc., AESF, Orlando, FL. (2002) 204
15) G. Palumbo, F. Gonzalez, K. Tomantschger, U. Erb and K. T. Aust, Plat. Surf. Fin., 90 (2) (2003) 36
16) U. Erb, G. Palumbo, R. Zugic and K. T. Aust, in Processing and Properties of Nanocrystalline Materials, C. Suryanarayana et al., (eds.), TMS, Warrendale, PA (1996) 93
17) K. T. Aust, U. Erb and G. Palumbo, in Processing and Properties of Nanocrystalline Materials, C. Suryanarayana et al., (eds.), TMS, Warrendale, PA (1996) 11
18) U. Erb, K. T. Aust, G. Palumbo, J. L. McCrea and F. Gonzalez, Processing and Fabrication of Advanced Materials IX, T. S. Srivatsan et al., (eds.), ASM International, Materials Park, OH (2001) 253
19) H. Gleiter, Progr. Mat. Sci., 33 (1989) 223