Industrial Applications of Nanocrystalline Electrodeposits

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Abstract

Nanocrystalline solids are an emerging class of advanced materials which have many improved properties compared with their conventional polycrystalline or amorphous counterparts. In recent years it has been shown that electrodeposition is a technologically and economically viable synthesis route to produce nanocrystalline metals, alloys and composites both in bulk form and as coatings. This presentation will address the synthesis, structure and properties of nanocrystalline electrodeposits. Industrial applications leading to new business opportunities for electroplating industries will be discussed.

Introduction

Nanocrystalline solids with grain size of less than 100 nm are a new and novel class of advanced materials which are currently receiving considerable attention in the scientific and business communities. Since their introduction in the early 1980's,[1] rigorous scientific activity in the areas of synthesis, microstructural characterization and property determination of these materials has resulted in the development of a number of manufacturing techniques capable of producing various materials with much improved properties over conventional materials.[2] Consequently, several industrial applications and hence new market opportunities have emerged from this field and are continuing to increase in numbers.

Most current efforts on large scale production of nanostructured solids are concerned with consolidating nanocrystalline precursor powders produced by techniques such as gas condensation, ball milling, or spray conversion.[2] Film deposition techniques such as physical and chemical vapour deposition, sol-gel techniques, etc. are also under intensive investigation.[2] Electroplating has been identified to be a technologically feasible and economically superior technique for the production of nanocrystalline pure metals and alloys as well as nano-composites.[3,4]

The following sections will deal with the structure-property relationship of nanocrystalline electrodeposits and highlight the advantages of electroplating over other synthesis techniques. Furthermore, a number of potential market opportunities will be discussed.

Synthesis and Structure

Generally speaking, any method capable of producing materials with ultrafine grains can be employed in the synthesis of nanocrystalline solids. However, over the past few years a number of processes have proven to be more feasible than others in terms of overcoming engineering barriers to mass production; these methods include inert gas condensation, ball milling and electroplating. While the former two produce particulates which will subsequently require consolidation, electroplating is capable of producing materials in both bulk form or as coatings with no post-processing requirements. It is interesting to note that the scientific community has initially ignored electrodeposition as a means of producing nanostructured materials, despite the fact that this approach is probably one of the oldest to synthesize such structures. Although there had been numerous reports in the literature on electrodeposits with ultrafine structures[eg.5,6], no systematic studies on the synthesis of nanocrystalline materials by electrodeposition methods to optimize certain properties by deliberately controlling the volume fractions of grain boundaries and triple junctions in the material by grains size reduction were published prior to 1989.[7,8]

Both direct current and pulsed current plating have been successful in producing a variety of nanocrystalline materials. Over the past few years, electrochemical processing windows for a number of pure metals (Ni[3], Co[9]), binary alloys (Ni-Fe[10], Co-W[11], Zn-Ni[3]), ternary alloys (Ni-Fe-Cr[12]) as well as metal matrix composites (Ni-SiC[3]) have been identified. The operating windows are selected such that the nucleation of new grains is favoured over the growth of existing grains during deposition. Such circumstances are brought about by careful selection of electroplating variables such as bath composition, pH, temperature, current density, duty cycle, etc..

Figure 1 shows a TEM darkfield and diffraction pattern for a nanocrystalline pure Ni specimen with an average grain size of 10 nm produced by pulse plating from a modified Watt's bath.[13] The grains are equiaxed with a very narrow size distribution. Furthermore, the electrodeposit is found to be free of porosity.[14] Negligible porosity in the deposit is a major advantage of electroplating over other synthesis techniques which produce particulates that require a subsequent consolidation process. Much effort is still required on particulate consolidation processes which yield products with low levels of porosity. Electrodeposition, on the other hand, produces the final product in one processing step.

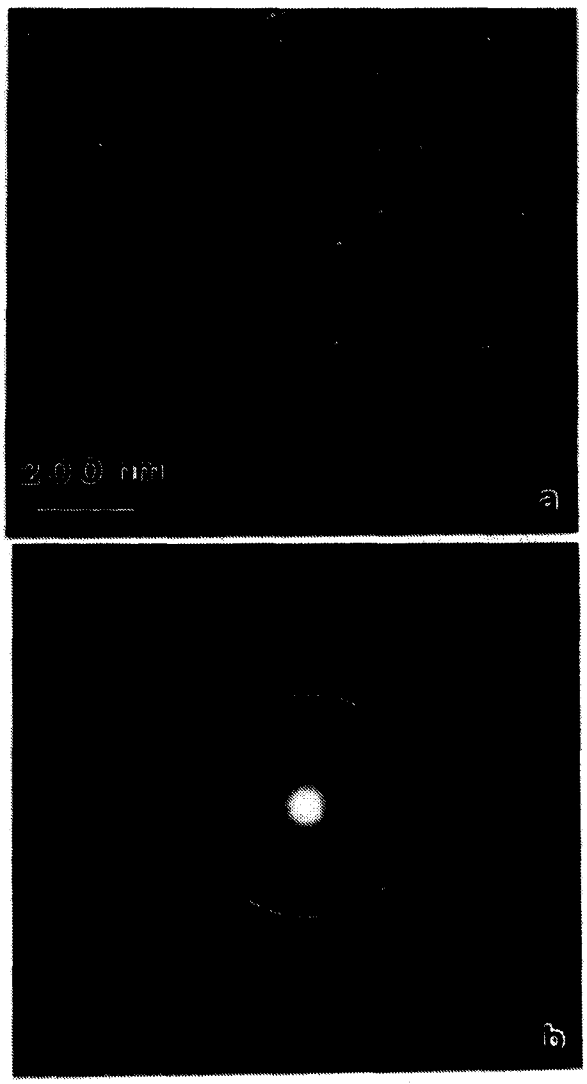

Figure 1 (a) TEM darkfield and (b) electron diffraction pattern of an electrodeposit with an average grain size of 10 nm.

As a result of considerable reduction in grain size over conventional polycrystalline metals, nanocrystalline solids contain far more grain boundaries and triple junctions which are though to be responsible for some of the unique properties of this class of materials. Based on theoretical considerations, Palumbo and co-workers[15] showed that the intercrystalline volume fraction (grain boundaries and triple junctions) increases from a value of 0.3% at a grain size of 1 μm to more than 50% at grain sizes less than 5 nm. Moreover, it was shown that the triple junction content exhibits a greater dependence on grain size than the grain boundary content such that they reach the same value at a grain size of approximately 2 nm.

There are other economically significant factors which make electroplating more attractive than other synthesis techniques such as gas-condensation. Transfer of technology from a research environment to the marketplace is easier in that low initial capital investment is required and fewer technological barriers need to be overcome. Electroplating is a mature technology with a well established infrastructure both of which are lacking for the gas condensation technique. Furthermore, gas condensation requires sophisticated vacuum technology which translates to high initial capital investment.

Properties

Property determination of electroplated nanocrystalline metals and alloys has revealed unique properties and improved performance over conventional materials of the same chemical composition. Increased hardness, improved corrosion and wear resistance, enhanced solid solubility as well as better soft magnetic properties make these metals and alloys ideal candidates for many industrial applications. Tables I and II summarize some of the properties studied for electroplated nanocrystalline nickel. Similar changes in other metal and alloy systems have also been observed. It should be noted that some properties where found to be strongly grain size dependent (Table I) while others were little affected by grain size (Table II).

Hardness

The hardness of bulk nanocrystalline nickel was found to be 5 times that of coarse grained Ni.[13] A hardness of 900 VHN for a 12 nm Ni-Fe-Cr alloy with composition close to Permalloy has been

Table I Properties of electrodeposited Ni nanocrystals which are strongly affected by grain size.

PROPERTY	OBSERVATION	Reference
Hardness	Increased by 5 times	13
Wear resistance	Increased by 170 times	16
Coefficient of friction	Reduced to ½	16
Localized corrosion	Nearly eliminated	17
Corrosion potential	shifted to more noble potential	17
Defect structure in passive layer	Higher defect density	18
Strength	Increased by 3 to 10 times	19
Ductility	Greatly reduced	19
Thermal stability	Greatly reduced	20,21,30
Solid solubility	Greatly enhanced	7,8
Hydrogen solubility	Greatly enhanced	22
Hydrogen diffusivity	Greatly enhanced	22,23
Coercivity	Single domain effects	24
Electrical resistivity	Increased by 3 times	25

Table II Properties of electrodeposited Ni nanocrystals which are little affected by grain size.

PROPERTY	OBSERVATION	Reference
Bulk density	Reduced by $< 1\%$	14
Thermal expansion	Unchanged	26
Young's modulus	Unchanged	27
Adhesion to substrate	Unchanged	28
Thickness of passive layer	same as for polycrystalline (1.3 nm)	18
Resistance to salt spray environment	Unchanged	28
Saturation magnetization	Reduced by $\approx 5\%$	24

reported.[10] Similar increases in hardness have also been observed for nanocrystalline Ni-P.[27] Figure 2 shows the hardness as a function of decreasing grain size for electrodeposited bulk Ni-P. The hardness initially increases with decreasing grain size and eventually levels off leading to considerable softening for deposits approaching the amorphous state. Similar trends have also been observed for other systems.[10,13] Many explanations for this behaviour have been offered but the to date the softening observed at the lowest grain size is still not completely understood.

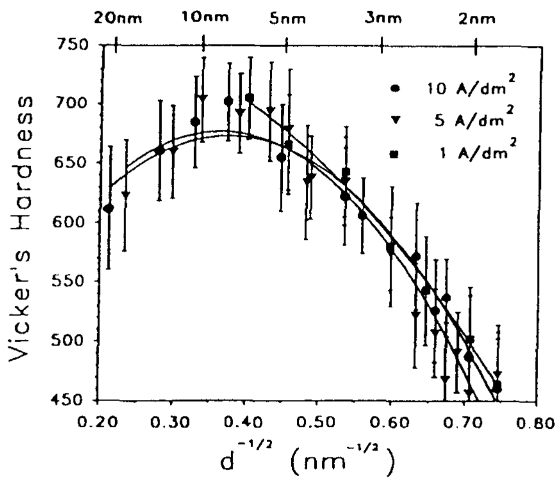

Figure 2 Hardness of electrodeposited bulk nanocrystalline Ni-P as a function of grain size.

Wear Resistance

Much improved wear resistance has also been observed as the result of grain size reduction into the nanocrystalline range. Electroplated nanocrystalline nickel with an average grain size of 10 nm produced by pulsed plating exhibits two orders of magnitude improvement in wear resistance in comparison to 1 μm grain size nickel.[16] Nanocrystalline metal matrix composites containing SiC, Al_2O_3 or other such particles are expected to have even more pronounced improvements in wear resistance.

Corrosion Resistance

Figure 3 shows the salt spray corrosion testing (ASTM B-117) results of nanocrystalline and conventional nickel electroplated onto mild steel substrates. The good corrosion resistance of conventional nickel is conserved in the nanocrystalline state.[28] Furthermore, potentiostatic and potentiodynamic corrosion testing have shown nanocrystalline nickel to be less susceptible to localized corrosion compared with its conventional coarse-grained counterpart.[17]

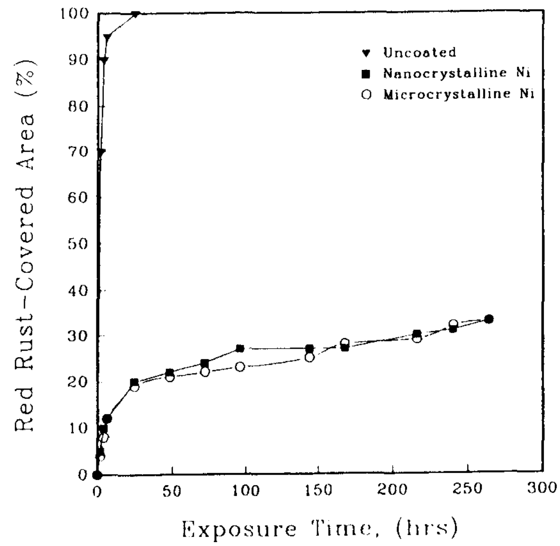

Figure 3 Results of salt spray corrosion testing of nanocrystalline nickel in comparison to bare steel and conventional nickel.

Extended Solid Solubility

As a result of considerable reduction in grain size, the associated increase in the defect density (i.e. grain boundaries and triple junctions) reaches significant proportions. Similarly, considerable broadening of the solid solubility range is observed. For example, solid solubility of P in Ni which, under thermodynamic equilibrium conditions, is almost zero at room temperature is increased to over 10 wt.% by nanoprocessing of Ni-P by electrodeposition.[7] Similar increases in solid solubility have also been reported for electroplated Co-W.[11]

Magnetic Properties

Thin films and bulk nanocrystalline materials with specific magnetic properties have been produced by various techniques, especially rapid solidification, gas condensation, and electroplating. Nanostructured materials could be used as soft magnets as well as permanent magnets.[2] Figure 4 shows the effect of decreasing grain size on the saturation magnetization of Ni produced by gas condensation as reported by Gong and co-workers[29] as well as electroplated Ni produced by Aus *et al.*.[24] It is believed that the decrease in saturation magnetization of nanocrystalline materials produced by gas condensation is due to the oxide layer which forms on each individual powder particle. However, in porosity free electroplated materials oxidation effects are negligible which explains the negligible decrease in saturation magnetization. Grain size independent saturation magnetization as achieved in electrodeposited nanocrystals is essential for soft magnetic applications.

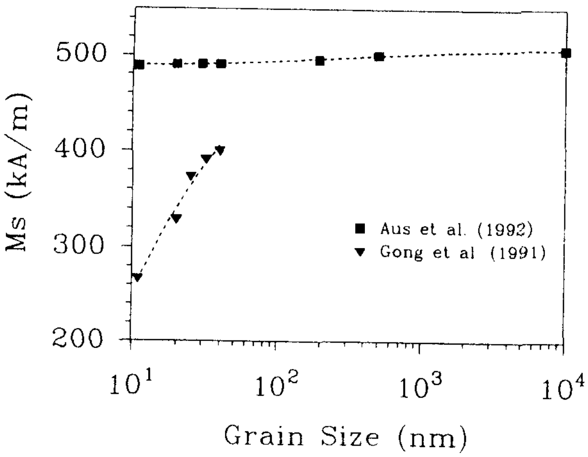

Figure 4 Saturation magnetization as a function of grain size.

Thermal Stability

As a result of the large interfacial component, nanocrystalline materials are in a metastable non-equilibrium state with a strong tendency to transform into a normal polycrystal with coarser grain size and reduced grain boundary and triple junction volume fractions. Unfortunately, the material may lose its improved or novel properties as a result of grain growth. Therefore, the thermal stability of nanocrystalline materials is of immense interest for industrial applications. Recent studies[30] have shown that electrodeposited nanocrystalline Ni with a starting grain size of 10 nm tend to become unstable at temperatures as low as 353K at which the onset of anomalous grain growth was observed. This resulted in a microstructure consisting of a few large grains within a matrix of nanocrystalline material. Uniform grain growth of all grains occurred at temperatures of 560K. However, small additions of phosphorus (≈ 1%) pushed to thermal stability to temperatures over 620K[20] which was explained in terms of Zener drag as a result of Ni_3P precipitate formation. Work is now in progress to increase the thermal stability limit to even higher temperatures by a combination of triple junction drag, solute drag and Zener drag.[20]

Applications

The emergence of electroplating as a viable technique for the production of many nanocrystalline metals and alloys with improved properties and performance will create new opportunities for this industry. The potential markets could affect many traditional companies, from job shops to the captive electroplating shops for electronic components. First, a detailed understanding of the effect of grain boundary and triple junction volume fractions on various properties is required. Here it must be kept in mind that different properties attain optimum levels at different grain size values and thus different interface contents in the materials. Once the individual structure-property-performance relationships have been established for a given material, electroplaters can utilize nanoprocessing to optimize certain desired properties for their customers. It should be noted that the extensive information on electrodeposits with ultrafine grain structure already known to the electroplaters' community could be of large help in this respect. A re-examination of these previous results in the light of recent advances in the understanding of grain boundary and triple junction volume fraction effects could provide a substantial basis for future work in this area.

Deliberate grain size control of electrodeposits can not only improve existing products but can also lead to new applications. The following sections summarize some of the applications which are presently under evaluation.

Corrosion and Wear Resistance Coatings

The improved hardness coupled with better corrosion and wear resistance make nanocrystalline electrodeposits ideal for protective coatings. These materials can also be used as hard facings on softer, less wear resistance substrates. Any part which is subject to wear such as electroformed printing mandrels will benefit enormously by the application of a layer of nanocrystalline metal. Such coatings will improve the life time of the mandrel, resulting in cost savings. Furthermore, as a result of enhanced solid solubility, electroplaters can offer their customers a wide range of new alloys which can not be produced by conventional means.

Heat Exchanger Repair

The application of nanocrystalline nickel and nickel alloys to combat intergranular stress corrosion cracking and other localized degradations in heat exchangers for the nuclear industry has been proposed.[12] These alloys can be plated on the inside of the tubes by an in-situ electroplating process to repair leaking tubes instead of using the more costly tube replacement option. A major Canadian utility company has recently successfully implemented first field trials of this electrosleeving technology at one of their nuclear power generating stations.

Data Storage

The magnetic and electrical performance displayed by nanocrystalline materials, combined with their excellent wear and corrosion resistance make them ideal contenders for the next generation of magnetic recording heads. These devices require materials with good soft magnetic properties, high electrical resistivity to reduce Eddy current losses as well as resistance to wear and corrosion for prolonged service.[31] Permalloy (Ni-20%Fe) which is extensively used by the magnetic recording head industry has recently been synthesized in the nanocrystalline form by electrodeposition[10] and is expected to have superior magnetic and electrical properties over the standards used today. Demand for faster and better data storage and retrieval is expected to multiply rapidly in today's data intensive society. Production of such high value added, advanced magnetic recording head devices could provide new high-tech opportunities for the electroplating industries.

Electronic Connectors

Materials requirements for electronic connectors include high corrosion and wear resistance, a dense, porosity-free barrier coating, hard and smooth surfaces as well as good solderability. A typical electrical connector today is plated with a layer of nickel and then a layer of gold or Ni-Pd. These combinations give the best corrosion and wear resistance, but require very expensive materials. A substrate of nanostructured Ni promises to give a harder, less porous surface requiring a thinner coating of gold. It may also be possible to replace Ni-Pd alloy with a less costly nanocrystalline alloy which does not require noble metals.

Catalysts

Recent studies have shown that nanocrystal processing may enhance the catalytic properties of materials. Trudeau *et al.*[32,33] have determined that nanocrystalline Ni-Mo alloys produced by mechanical alloying are more electro-active than conventional polycrystalline Ni-Mo alloys. It was determined that the overpotential of the cathodic hydrogen evolution reaction (HER) in high temperature caustic media was reduced considerably. Doyle *et al.*[34] have further investigated the cathodic polarization behaviour of nanocrystalline Ni electrodeposits and determined the catalytic activity to be significantly enhanced relative to conventional Ni. This was attributed to the large volume fractions of interfaces which provide active sites for the hydrogen evolution reaction. Thus, nano-processed HER electrodes of superior electrocatalytic properties could be produced.

An alkaline water analysis cell generates hydrogen and oxygen from water by consuming electricity. The opposite process is utilized in an alkaline fuel cell which produces electricity by a direct electrochemical conversion of hydrogen and oxygen into water. Therefore, the potential catalyst systems for hydrogen consumption fuel cell anodes are essentially identical to those for the hydrogen evolution reaction cathodes. Significant improvements are expected by nano-processing of these anodes.

Aerospace and Automotive Coatings

Work has been initiated to evaluate the replacement of hexavalent chromium and cadmium plating on hydraulic pistons, landing gear components and automobile shock absorbers with nanocrystalline alloys. In these applications the drive is environmental, where much more stringent workplace and emission / effluent standards are putting pressure on chromium and cadmium. In North America these regulations still permit the use of these materials while in some European countries, materials such as cadmium have been banned. Companies who wish to market world products must take into account the environmental regulations in all markets.

Conclusions

Electroplating has been shown to be a technically feasible method of production for a wide range of metals, alloys and composites in the nanocrystalline form. Research on the structure-property-performance relationships of these materials has revealed many interesting properties which can be exploited for commercial purposes. Many commercialization efforts are under way for the mass production of these materials. Of all the nanoprocessing techniques, electroplating appears to be one of the most promising in that it is a relatively low cost and more flexible process for producing materials both in bulk form or as coatings on other substrates. Consequently, new markets and business opportunities are expected to emerge for the electroplating industry.

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