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ELECTRODEPOSITED NANOSTRUCTURED FILMS AND COATINGS: SYNTHESIS, STRUCTURE, PROPERTIES AND APPLICATIONS

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1. Introduction

Major advances in materials design are often the result of innovation in material synthesis and processing technologies. For example, over the past three decades, enormous progress has been made in the development of novel electronic materials and devices after vacuum technology and various thin film deposition methods had reached the level of sophistication that enabled the synthesis of extremely thin layers of metals, dielectrics, semiconductors and insulators. Here, the precise control of thickness, defect structure and chemical composition of the materials were of utmost importance and required unique solutions in processing technology. In contrast, other advanced materials of high innovation potential can be derived from a particular premise to achieve desirable structure-property-performance relationships in the material through microstructural design. The synthesis methods to achieve innovation in these materials are then often of secondary concern; they may still be novel but in many cases they are simply modifications of well-established and mature technologies.

A good example for advanced materials falling into the latter category are nanostructured materials. This field was first introduced by Gleiter [1] almost two decades ago. The original premise in Gleiter's approach was to synthesize a new solid state structure – an interfacial material – which differs from the crystalline and amorphous counterparts of the same chemical composition. Gleiter's proposal to achieve such a new structure by introducing very large volume fractions of grain boundary or interface atoms by crystal size reduction was based on the understanding of grain boundary structure – property relationships at that time. If one further considers that "not all grain boundaries are created equal" [2] (i.e. their structure and properties depend greatly on the misorientation between adjacent grains) one can categorize fully dense nanostructured materials as a subgroup of grain boundary engineered (GBE) materials. The innovation in GBE materials is then the precise engineering of average grain size, grain boundary volume fraction and character distribution for desired application-specific material performance. In other words, by controlling the type and / or volume fraction of grain boundaries of conventional engineering materials, using modifications

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of existing processing technology (such as thermomechanical processing, ball milling, rapid solidification, electrodeposition), unique material performance characteristics in bulk materials as well as films and coatings can be achieved.

This paper deals with electrodeposited nanostructures. After reviewing the chemistry and physics involved in the synthesis of these materials, a brief summary of some of the unique mechanical, physical and chemical properties will be given. Several practical applications of these materials will also be presented.

2. Synthesis

Electrodeposition is a low temperature processing route to produce nanostructured materials, most often in a single step requiring no secondary consolidation. Usually 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 leading to nanocrystals have been previously published for pure metals (e.g. Ni [3-5], Co [6], Pd [7], Cu [6]), binary alloys (e.g. Ni-P [8, 9], Ni-Fe [10], Zn-Ni [11], Pd-Fe [12], Co-W [13]) and ternary alloys (e.g. Ni-Fe-Cr [14, 15]). Even multilayered or compositionally modulated alloys (e.g. Cu-Pb [16], Cu-Ni [17, 18], Ag-Pd [19], Ni-P [20]), metal matrix composites (e.g. Ni-SiC [3]), ceramics (e.g. ZrO_2 [21]) and ceramic nanocomposites (e.g. $Tl_a Pb_b O_c$ [22]) have been successfully produced by electrodeposition methods.

Electrocrystallization occurs either by the build up of existing crystals or the formation of new ones [23]. 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 [23, 24]. The other important factor in nanocrystal formation during electrocrystallization is overpotential [23, 24]. Grain growth is favoured 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 often negligible [e.g. 25].

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 are listed in table 1 and Fig. 1.

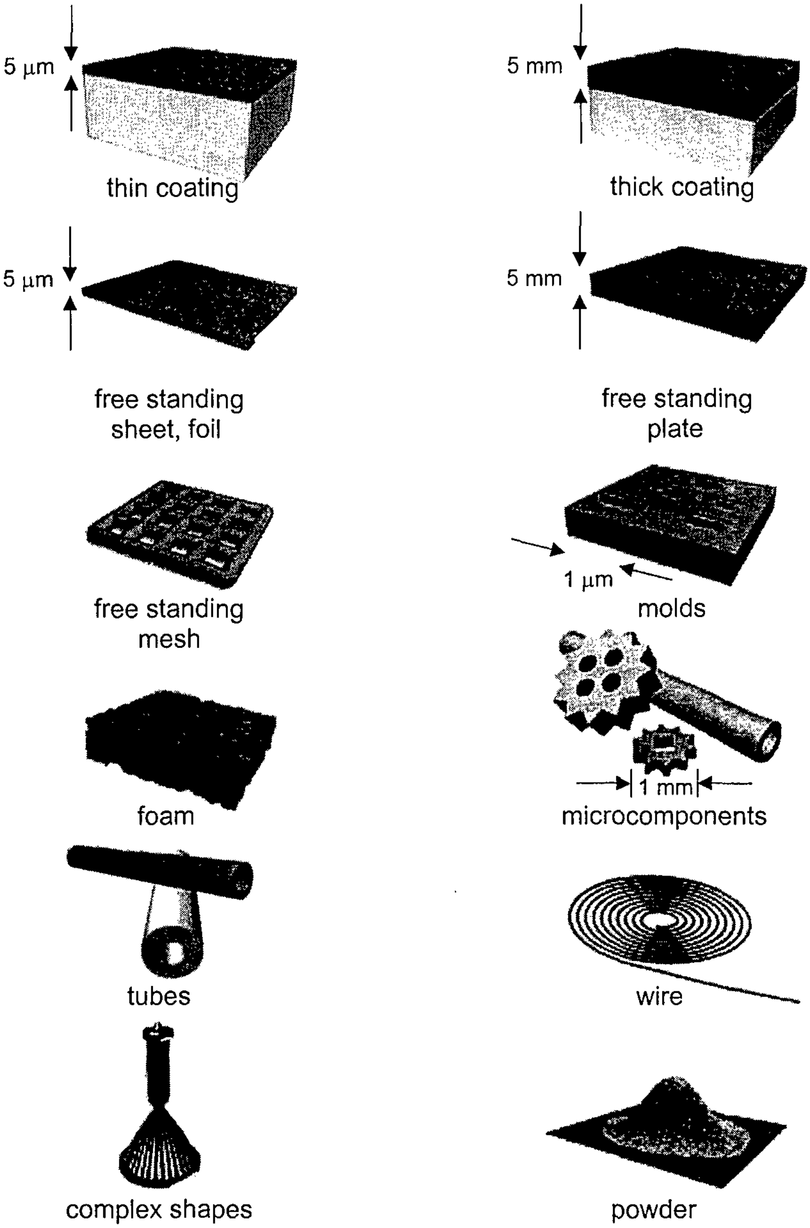

Figure 1.Various shapes of electrodeposited products

TABLE 1. Various Shapes and Applications of Electrodeposited and Electroformed Products

Shapes	**Applications**
Thin Coatings (on Substrate)	Surface Modification for Wear and Corrosion Resistance; Catalytic Surfaces
Thick Coatings (on Substrate)	Electrosleeve™; Repair of Worn Components
Sheet, Foil (Free-Standing)	Gaskets; Pressure Control Membranes; Hydrogen Purification Membranes Thermal Barriers; Solar Energy Absorbers; Microfoils; Soft Magnets
Tubes, Wire (Free-Standing)	Surgical Tools; Missile Guidance Systems; Miniature Gamma Radiation Sources
Mesh (Free-Standing)	Filters; Precision Sieve Screens; Razor Foils; Printing Screens; Centrifuge Screens
Plate (Free-Standing)	Structural Applications
Foam (Free-Standing)	Filters; Electromagnetic Shielding; Battery Electrodes; Catalyst Carriers
Molds (Free-Standing)	CD Stampers; Embossing Tools for Holograms; Compression, Injection and Pattern Molds
Free Forms	Precision Bellows; Erosion Shields for Helicopters; Thrust Chambers for Rocket Engines; Components for Micro-magnetic Motors, Microoptics, Microactuators and Microfiltration; Shaped Charge Liners; Precision Reflectors and Mirrors; Nozzles.
Powder	Catalysts; Reinforcements

The Electrosleeve™ applications will be discussed in section 5. 1.

3. Structure

In the as-plated condition electrodeposited nanocrystals are fully dense materials, usually with negligible porosity [26, 27] unless they are deliberately produced in powder form. They are non-equilibrium structures which is primarily manifested in the small crystal size and the associated large volume fraction of grain boundaries and triple junctions [28, 29] and considerable extension of the solid solubility range as observed, for example, in Ni-P [8, 9], Zn-Ni [11] and Ni-Mo [30]. Grain size distributions are usually very narrow exhibiting log normal behaviour and average grain size and crystallographic texture can be controlled by various plating parameters, for example bath pH, current density, etc., [31]. High resolution electron microscopy has revealed that the grain boundary structures in electrodeposited nanocrystals are similar to the structures found in conventional polycrystalline materials [32]. Cross-sectional examination of thin (~ 2.5 μm) and thick (>1mm) coatings has shown that the nanocrystalline structure is fully established right at the interface with the substrate and that the grain size is essentially independent of coating thickness [33]. This is in contrast to conventionally produced electrodeposits which often show considerable grain coarsening with increasing coating thickness [34]. Purities of 99.9% or better can be achieved by proper bath control and choice of electroplating parameters.

4. Properties

A comparison of the microstructures of nanomaterials produced by consolidation of precursor nanocrystalline powders and electrodeposition shows that the main difference is the porosity in the final product; porosity usually being negligible in electrodeposited nanocrystals. Consequently, considerable differences in some properties have been observed in both groups of materials [see e.g. 35]. For example, the initially reported large changes in Young's modulus, thermal expansion, specific heat, saturation magnetization and Curie temperature observed on consolidated nanocrystals were not found in electrodeposited nanostructures. In fact, the grain size independence of saturation magnetization and Curie temperature are fully consistent with the results of recent first principle calculations which showed that the magnetic moment of atoms in grain boundary structures is not strongly affected by the structural disorder associated with various boundary types [36]. It has been concluded [35] that the differences in certain properties measured on consolidated and electrodeposited nanostructures were mainly due to porosity and associated impurity effects rather than the presence of large volume fractions of grain boundaries and triple junctions.

What is commonly observed in both groups of materials, however, are the remarkable improvements in hardness, yield strength, ultimate tensile strength and wear rate. For example, table 2 shows a comparison of some mechanical properties of conventional polycrystalline and two grades of nanocrystalline Ni with 100nm and 10nm grain size, respectively. Fig. 2 shows the hardness as a function of grain size in the usual Hall-Petch [37, 38] plot for nanocrystalline Ni. The observed transition from regular to inverse Hall-Petch relationship has also been observed for Ni-P [29], Ni-Fe [10] and Ni-Mo [30] alloys. The corresponding reduction in the dry wear rate for Ni from about 130×10^{-5} mm^3/mm at an average grain size of 10μm to an extremely low value of

$0.8x10^{-5}$ mm^3/mm at 10nm grain size is shown in Fig. 3, together with the concurrent decrease in the coefficient of friction [39]. In nanocrystalline Ni-1% P alloys (10nm grain size) the hardness can be further increased from about 700 VHN in the as-plated material to over 1200 VHN by appropriate annealing treatment (400°C, 20 minutes) as shown in Fig. 4 [40]. The increase in hardness was found to be the result of grain growth to 30nm and simultaneous formation of Ni_3P precipitates as per equilibrium phase diagram [41]. Further annealing at 400°C as well as annealing at 500°C and 600°C resulted in excessive microstructure coarsening indicated by a decrease in hardness.

TABLE 2. Mechanical Properties of Conventional and Nanocrystalline Nickel

Property	**Conventional** [a]	**Nano-Ni**	
		100nm	**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	0.0
Fatigue Strength, MPa (10^8 cycles/air/25°C)	241	275	-
Wear Rate (dry air pin on disc), $\mu m^3/\mu m$	1330	-	7.9
Coefficient of Friction (dry air pin on disc)	0.9	-	0.5

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

The corrosion behaviour of nanocrystalline Ni has been extensively studied using potentiostatic and potentiodynamic polarizations in various corrosive environments (2N H_2SO_4 solution [pH=0], 30-wt% KOH solution [pH=13] and 3wt% NaCl solution [pH=7]) [30, 42-44]. It has been demonstrated that, as far as overall corrosion rate is concerned, the excellent corrosion performance of Ni is not compromised significantly by grain size reduction. These tests, together with further corrosion tests (ASTM G28 – susceptibility to intergranular attack; ASTM G35, G36 and G44 – susceptibility to stress corrosion cracking) have shown that nanostructured Ni is intrinsically resistant to intergranular attack and intercrystalline stress corrosion cracking [45]. The material was also found to be resistant to pitting attack and only slightly susceptible to crevice corrosion (ASTM G48) [45].

Nanocrystalline Ni electrodeposits having an average grain size of 20nm are also observed to display higher electrocatalytic behaviour when compared to cold worked, fine grained and fully annealed reference structures, with regards to the hydrogen evolution reaction (HER) for alkaline water electrolysis at room temperature [46]. The enhanced HER kinetics observed here are considered to be the direct result of the high area fraction of grain boundaries (and to some extent, triple junctions) which

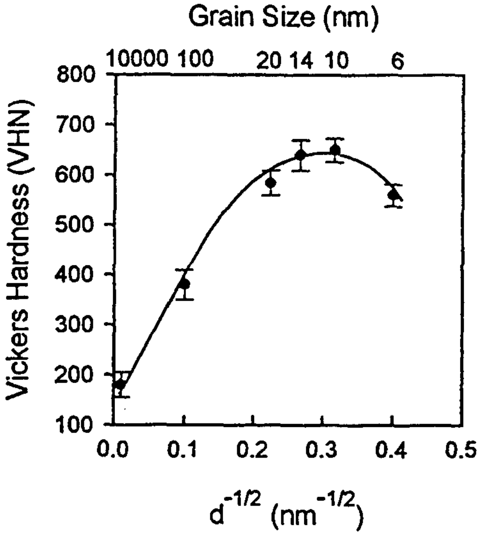

Figure 2. Hardness of nanocrystalline Ni a function of grain size [31]

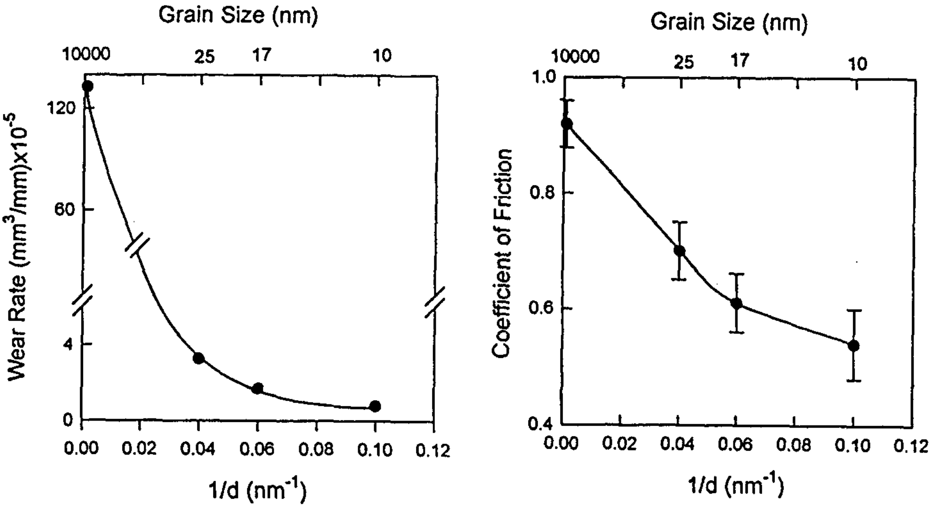

Figure 3. a) Wear rate of Ni electrodeposits as a function of grain size [39].
b) Corresponding coefficients of friction [39].

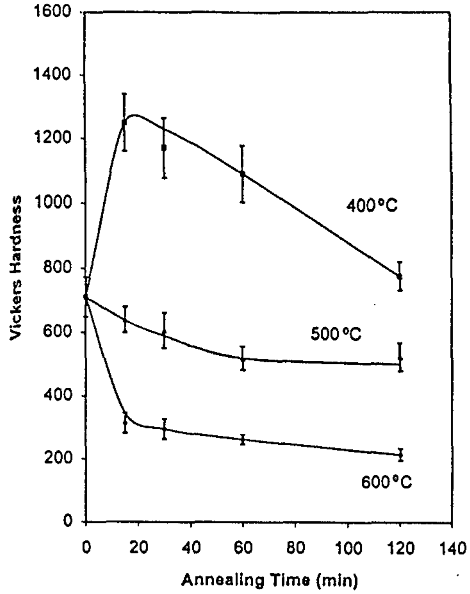

Figure 4. Hardness of nanocrystalline Ni – 1%P having a starting grain size of 10nm as a function of annealing treatment [40].

intersect the free surface of the electrode. It has been further shown [30] that the HER kinetics can be further enhanced by alloying nanocrystalline Ni with molybdenum.

5. 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 since, as has been outlined in previous section, many of the extraordinary 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. In this section, an overview of some current and emerging practical applications for electrodeposited nanocrystalline materials are presented and discussed in light of the importance of property-specific grain size 'optimization' rather than grain miniaturization for its own sake.

5. 1. 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– the Electrosleeve™ process for in-situ repair of nuclear steam generator tubing [47]. This proprietary process [48] has been successfully implemented in both Canadian CANDU and U.S. Pressurized Water Reactors, and has been incorporated as a standard procedure for pressure tubing repair [49]. In this application, nanocrystalline Ni (100nm) is electroformed as a thick coating (0.5–1mm) on the inside surface of steam generator tubes to effect a complete structural repair at sites where the structural integrity of the original tube has been compromised (e.g., corrosion, stress corrosion cracking etc.). The high strength and good ductility of this 100nm grain size material (see table 2) permits the use of a thin 'sleeve' (0.5-1mm) which minimizes the impact on fluid flow and heat transfer in the steam generator.

Recent geometric models and experimental findings [50, 51] 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.); applications in which durability and performance are frequently compromised by premature intergranular failure.

5. 2. FUNCTIONAL APPLICATIONS

Some of the most promising industrial applications for nanostructured materials are in the area of soft magnets for high efficiency transformers, motors, etc. Anticipated reductions in magnetocrystalline anisotropy and coercivity as grain size is reduced below the mean thickness of a magnetic domain wall in conventional materials, have generated considerable development activity in this area. The main advantage of electrodeposited nanocrystals is their uncompromised saturation magnetization. The industrial use of these high performance ferromagnetic materials in motor, transformer and shielding applications has been accelerated by the recent development of a drum plating process for cost-effectively producing large quantities of sheet, foil, and wire in nanocrystalline form.

Another 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. For this application grain size has been optimized on the basis of calculated electrical resistivity for nanocrystalline Cu [52]. A 50nm to 100nm grain size provides optimum etchability while maintaining good electrical conductivity.

As has been previously discussed, the high density of intercrystalline defects present within the bulk, and intersecting the free surface of nanostructured materials provides considerable opportunity in catalytic and hydrogen storage applications. Several applications are being developed for the use of these materials, either as an electrodeposited coating or electroformed free-standing component in Nickel Metal Hydride battery systems, and as alkaline fuel cell electrodes.

5. 3. 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 coatings. Examples include hard facing on softer, less wear resistant substrates, recording heads, electronic connectors, replacement coatings for chromium and cadmium in automotive, aerospace, and defense applications, in particular for non line-of-sight applications such as crevices, angles, bores, etc. In the latter application the drive is primarily environmental, where much more stringent workplace and emission / effluent standards are putting pressure on hard chrome and cadmium plating. In North America, these regulations still permit the use of these materials but in some European Countries, materials such as cadmium have already been banned.

6. Fully Grain Boundary Engineered Nanostructures

Until recently the primary GBE concept applied to electrodeposited nanocrystals was the consideration of the grain boundary and triple junction volume fraction enhancement by grain size reduction. The structure-property relationships presented in the previous sections were mainly for nanostructures in the as-plated conditions with little consideration of the second concept of grain boundary engineering – the grain boundary character distribution. For conventional polycrystalline materials, the optimization of grain boundary character distribution to achieve a high population of low Σ CSL (Coincidence Site Lattice) boundaries has recently emerged as a technically viable and cost-effective means of achieving significant performance improvements (e.g. enhanced ductility, creep resistance, fracture resistance) in practical engineering materials [53]. For polycrystalline materials it has been shown that mobility differences between low Σ and general grain boundaries during grain growth can be used to optimize conventional metallurgical thermomechanical processes in order to achieve significant increases in the population of low Σ CSL boundaries [54]. In order to assess the possibility to achieve high frequencies of special boundaries in nanocrystalline materials by annealing, a series of experiments have been conducted on nanocrystalline Ni-15wt% Fe having an initial average grain size of 30nm. Specimens were annealed at 600^0C for annealing times in the range of 5s to 900s and subsequently analyzed by electron backscatter diffraction [54]. Preliminary results from this analysis as shown in Fig. 5 are very encouraging. The low Σ CSL population is shown to initially increase with increasing grain size in the range of 150nm to 300nm and then subsequently decrease with increasing grain size in the range 300nm to 7μm.

Further experimentation is currently underway to (1) extend measurements to grain sizes below 100nm, (2) evaluate the effect of annealing temperature on the phenomenon, (3) to observe if similar effects can be observed with other nanocrystalline electrodeposits and (4) to evaluate the effect of optimized grain boundary character distribution in nanocrystals on the materials performance.

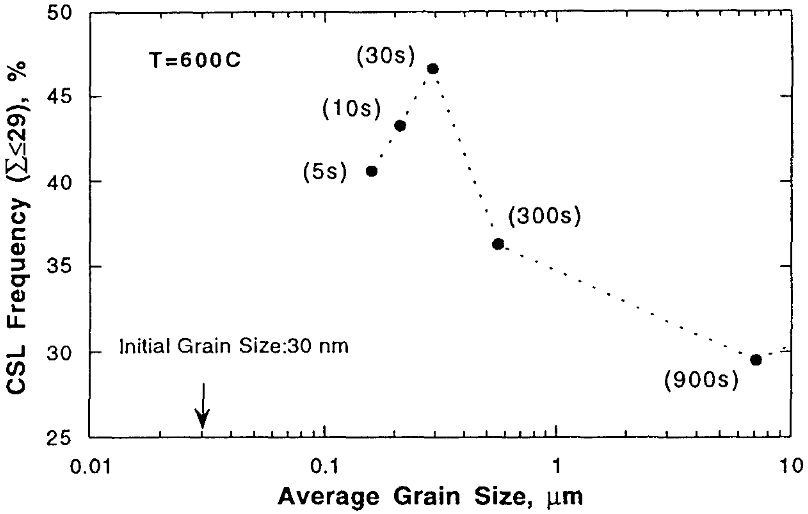

Figure 5. CSL frequency as a function of average grain size for Ni – 15%Fe. Values in parentheses present annealing times [54].

7. Conclusions

Electrodeposition of fully dense nanocrystalline materials can be considered a distinct form of grain boundary engineering resulting in interfacial materials containing large volume fractions of grain boundaries and triple junctions. Materials produced by electrodeposition exhibit excellent mechanical, wear, corrosion, catalytic and magnetic properties. Several economically viable electrodeposition technologies are already available to produce large quantities of various pure metals, alloys and composites in many different forms and shapes including thin and thick coatings, free-standing foil, sheet, tubes and wires as well complex geometries. Post deposition annealing of nanostructured electrodeposits is proposed as a means of optimizing grain boundary character distributions which could result in further property improvements of these materials.

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