Electrodeposited Nanocrystalline Coatings for Hard-Facing Applications

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In this presentation, the synthesis, structure and properties of electrodeposited nanocrystalline and nanocomposite materials are reviewed in the light of emerging hard-facing applications. As a result of extreme grain refinement and corresponding Hall-Petch strengthening, metals, alloys and metal-matrix composites (e.g., Co-, Ni- and Febased alloys) can have their hardness increased 4- to 5-fold by grain size reduction into the nanometer size range (i.e., 3-100nm). Moreover, these increases in hardness are achieved with minimal compromise in ductility. These nanoscale coatings are shown to provide a versatile, cost-effective and environmentally-benign alternative to current hard coating technologies (e.g., hard chromium plating, HVOF, etc.).

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INTRODUCTION

Hardfacing coatings see extensive use in numerous industrial applications. These coatings require a high intrinsic hardness (600-1000 VHN) and low friction coefficient (<0.20) in order to impart excellent wear performance. Although several non-aqueous coating technologies (e.g. HVOF, etc.) are currently in various stages of development and commercial application, the most widely applied hard facing coating is electrodeposited chromium (5 to 250µm thick), which continues to be used extensively in both industrial and military applications. The most common (and most practical) means of depositing such hard chromium deposits has been through the use of chromic acid baths. Health risks associated with the use of hexavalent chromium baths have been recognized since the early 1930's [1]. Although significant progress has been made in the development of less harmful 'trivalent Cr' plating processes [2], a reliable industrial process has yet to emerge.

In addition to the health risks associated with Cr plating, there are several other technical drawbacks to this technology. As a result of the relatively low electrolytic efficiency of Cr plating processes, deposition (or build) rates are relatively low compared to the plating of other metals and alloys (e.g., 25-50µm per hour for Cr versus > 200µm per hour for nickel) [3]. As a further consequence of this low Cr-plating efficiency, high rates of hydrogen co-generation occur and precautions must be taken to prevent hydrogen embrittlement of susceptible substrate materials (e.g., high strength steels). Moreover, the intrinsic brittleness of hard chromium deposits (i.e., <0.1% tensile elongation [4]) invariably leads to micro or macro-cracked deposits. These 'cracks', which do not compromise wear and erosion resistance, are wholly unsuitable for applications where corrosion and fatigue resistance is required.

Electrodeposited nanocrystalline metal and alloy coatings, possessing extreme grain refinement to the 3-100 nm size range, in addition to being fully compatible with current hard chromium plating infrastructure, have displayed properties that may render them a superior alternative to hard chromium coating technology. Over the past decade, electrodeposited nanostructures have advanced rapidly to commercial application because of the following factors: 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. From the outset, the fully dense nanomaterials 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 the present paper an overview is presented of the current status of electrodeposited nanocrystalline materials as an alternative hard-facing coating technology.

NANOCRYSTALLINE METAL AND ALLOY COATINGS

Conventional electrodeposition parameters (e.g. bath composition, pH, temperature, overpotential, bath additives, etc.), as outlined in US Patent Nos. 5,352,266 and 5,433,797, can be modified and optimized to yield deposits with grain sizes below 100nm [5,6]. These coatings can be produced with deposition rates in excess of 150 μ m/h and at current efficiencies greater than 95%. The latter being of particular relevance to the alleviation of hydrogen embrittlement concerns when depositing on susceptible substrates (e.g., high strength steels).

As a result of Hall-Petch strengthening, nanocrystalline materials display significant increases in hardness and strength relative to their coarser grained counterparts. Hardness increases on the order of 500% to 700% have been typically observed [7-12]. Deviations from Hall-Petch behavior have been noted at extremely fine grain sizes (i.e., <20nm) and attributed to the breakdown of dislocation pile-up mechanisms [12] and the potential for alternative 'softening' mechanisms such as room temperature Coble creep [8] and triple line disclination processes [7,13].

Table 1 summarizes the nanocrystalline grain sizes and corresponding hardnesses achieved to date by modification of several 'simple' electrodeposition systems for common metals and alloys. Although very high hardness values are obtainable, the deposits retain considerable ductility and do not display microcracking, as is frequently observed in other hardfacing coatings (e.g., chromium).

TABLE I: TYPICAL HARDNESS VALUES ACHIEVED WITH		
ELECTRODEPOSITED NANOSCALE MATERIALS		
Chemical	Avg. Grain Size (nm)	Hardness (VHN)
Composition		
Ni	11	660
Ni-7wt.%Mo	14	620
Ni-0.5wt.%P	<5	>1100
Ni-20wt.%Fe	15	690
Ni-15wt.%Cr-	12	800
10wt.%Fe	12	890
Со	13	650
Co-1wt%P	< 10	680
Co-5wt%P	< 10	745
Co-30wt%Fe-3wt%P	15	890
Co-45wt%Fe-	10	650
10wt%Zn		
Co-12wt.%W	<100nm	550
Zn-13wt.%Ni	60	425
Zn-20wt%Ni	<100nm	540

The correlation between wear performance and material hardness is given by Archard's Law [14], which demonstrates that the volume loss due to wear should be inversely proportional to the hardness of the material. The applicability of this law to nanocrystalline materials has been recently demonstrated by Jeong et al [15] where the grain size dependence of wear performance was examined using the commonly used Taber test technique [16].

Figure 1(a,b) shows the effect of average grain size on both the hardness and Taber wear index (a measure of volume loss due to wear) for nickel. As shown, decreasing the grain size of Ni from 90μ m to 13nm results in hardness increases from 125 to 625VHN; commensurately, the Taber Wear Index is reduced from approximately 37 to 21.



Figure 1. (a) Hardness as function of grain size for Ni. (b) Taber wear index as function of grain size for Ni [15].

Figure 2 shows the Pin-on-Disk (POD) volume wear loss for various nanocrystalline Co alloys relative to those obtained with mild steel, tool steel and hard chrome. As noted in this figure, the wear resistance is no longer a simple function of the material hardness. When tested under identical conditions, the wear resistance of most of the nanocrystalline deposits exceeded that of hard chrome, even though their hardness values were lower. The POD volume wear loss values for nanocrystalline cobalt decrease with the addition of phosphorus and with precipitation hardening. The addition of iron results in a further decrease in the wear loss.

It is important to note that although the wear performance of these single phase nanocrystalline coatings currently only approaches that of hard chrome, there exist significant benefits possessed by these nanocrystalline coatings, which already render them a superior alternative for specific applications. For example, the significant ductility of nanocrystalline materials relative to hard chromium, and the absence of microcracking, provides significant advantages in fatigue and corrosion performance. Also, the high current efficiencies associated with the deposition of these nanocrystalline materials mitigates problems associated with hydrogen embrittlement. Moreover, as outlined in the next section, these nanocrystalline single phase systems can provide a hard but ductile matrix for incorporation of second phase particles which can impart even greater hard-facing improvements.



Figure 2. Pin-on-disk (POD) wear loss values for various nanocrystalline materials along with mild steel, tool steel and hard chromium. The Vicker's microhardness value is given on top of the bar for each material on the chart.

NANOCOMPOSITES

Further increases in hardness, and wear resistance may be achievable through the incorporation of second phase particulates in the nanocrystalline metal/alloy matrix. One approach is alloy deposition followed by heat treatment to precipitate a finely dispersed second phase. Figure 3 shows precipitation hardening in the nanocrystalline cobalt-iron-phosphorus alloy, whereby hardness is plotted as a function of annealing time at 300, 400 and 500°C for up to 100 hours. The Co-Fe-P deposit shows an increase in hardness with annealing time at all temperatures, passing through a maximum after approximately 1 hour, followed by a slow decrease with increasing time. It should be emphasized at this point that through a short heat treatment process, the presence of phosphorus in the deposit results in an additional increase in hardness to values close to those for the upper limit of hard chromium. A similar trend has also been observed for electrodeposited nanocrystalline nickel-phosphorus alloys [17]. The subsequent decrease

in hardness is believed to be due to the over-ripening of the precipitates. The additional loss in hardness during annealing at 500°C to values below that of the as-deposited material is due to the onset of grain growth, resulting in a loss of the Hall-Petch strengthening.



Figure 3. Effect of annealing time at 300, 400 and 500° C on the hardness of a nanocrystalline Co-Fe-P alloy.

Nanocomposite coatings can also be produced by co-deposition during the electroplating process, whereby the second phase particulate is kept in suspension in the plating bath. In this manner, insoluble second phases of metal, alloy, ceramic or polymer can be uniformly distributed in the host nanocrystalline metal or alloy matrix. Figure 4a shows an example of nanocrystalline nickel (13nm avg. grain size) containing a uniform dispersion of aluminium oxide particles (approx. 1 μ m in diameter), produced by electrodeposition. Figure 4b presents a bright field TEM image of two AbO₃ particles and the surrounding nanocrystalline matrix showing that the nanocrystalline matrix structure continues up to the particle/matrix interface.



Figure 4. (a) Scanning electron micrograph (backscattered electron image) of nanocrystalline nickel (20nm average grain size) matrix containing $1\mu m Al_2O_3$ particulate (black), (b) Bright field TEM micrograph of nanocrystalline Ni-Al_2O_3 deposit showing the interface between the matrix and the Al_2O_3 particle.

The benefits of utilizing a nanocrystalline metal-ceramic composites is shown in Figure 5 for Ni-SiC. Significant increases in hardness, yield strength and ultimate tensile strength are achieved by utilizing a nanocrystalline rather than a conventional nickel matrix. In this work [18], it was also noted that the nanocrystalline composite possessed significantly improved ductility.



Figure 5. Summary of mechanical properties for Ni–SiC composites produced by electrodeposition [18].

In addition to the potential for incorporating hard second phase particles, there exists the opportunity to also incorporate second phases with functional properties. For example, hard-facing coatings with self-lubricating properties could be highly desirable in certain applications. Such properties could be achieved through the use of dry lubricant particles such as graphite, PTFE etc. Such co-deposited systems are already commercially available with a conventional grain size matrix (e.g., Ni). However, the use of a hard nanocrystalline matrix extends the applicability of these coatings to more severe industrial applications, since by application of the rule of mixtures, the relatively 'soft' lubricating second phase can be incorporated to larger volume fractions without significant compromise of the overall hardness of the coating.

Figures 6a and 6b show parallel and through-thickness SEM micrographs, respectively, of a nanocrystalline Ni-P matrix containing hexagonal boron nitride (BN) particles (mean particle size $\sim 10\mu$ m). The presence of the BN particles in the material results in a coating that 'self-lubricates' during wear. Figure 7 shows a photograph of hydraulic expansion mandrels, coated with a nanocrystalline Ni-MoS₂ composite, which utilize the self-lubricating mechanism in order to extend their service life.



Figure 6. Parallel (a) and through-thickness (b) SEM micrographs of a nanocrystalline Ni-P matrix with BN particles.



Figure 7. Self lubricating nanocrystalline nickel + molybdenum disulfide composite coating on hydraulic expansion mandrels.

SUMMARY

Nanocrystalline metals and alloys produced by electrodeposition, show considerable promise as alternative hard-facing coating materials as a result of their high hardness and wear resistance. Further advances in the commercial development of these materials are expected from the co-deposition of nano-composites whereby the addition of a second phase to the nanocrystalline materials can provide further strengthening and/or functional properties such as enhanced lubricity.

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