Synthesis, Structure and Properties of Nanocrystalline Nickel-Phosphorus Electrodeposits

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Abstract

Ni-P alloy deposits were the first electroplated nanocrystalline metals to be studies in detail since the early 1980's. Numerous fundamental and applied studies have dealt with the synthesis, microstructural evolution as a function of plating parameters, and various properties of such deposits. This review paper summarizes recent advances in the understanding of nanocrystalline Ni-P deposits produced from plating solutions very similar to the baths originally described by A. Brenner. The effects of grain size (<100 nm) and/or deposit phosphorus content on the mechanical properties (Young's modulus, hardness, Taber wear index), corrosion behavior, thermal stability and saturation magnetization will be discussed. The structural and property transitions observed between nanocrystalline and amorphous deposits will also be addressed.

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1. Background

Nickel-phosphorus alloy electrodeposits have been described in numerous studies for more than 50 years [e.g.1,2]. Our work over the past two decades on nanocrystalline Ni-P electrodeposits was inspired by the studies of two particular groups: Brenner et al. [e.g. 3] and Bestgen and co-workers [4-6]. Brenner and coworkers showed that Ni-P electrodeposits go through a structural transition from crystalline to amorphous when the phosphorus content of the alloys is increased. Most of their structural studies were based on X-ray diffraction and line broadening analysis. Bestgen et al. performed transmission electron microscopy studies and described electrodeposition conditions leading to what was described as microcrystalline electrodeposits, in addition to amorphous structures.

During the early years of research on nanocrystalline materials (1980-1990), many new techniques for the synthesis of these unusual structures were introduced including inert gas condensation, mechanical attrition, crystallization of amorphous precursor materials, etc. [e.g.7]. It was during the early 1980's when we began to study electrodeposition as a means of producing nanocrystalline materials, alloys and composites. Using Ni-P electrolyte formulations very similar to the baths described by Brenner, the full range of microstructural transitions-from normal crystalline to amorphous-was systematically studied using a combination of X-ray diffraction and transmission electron microscopy [8, 9].

Our work on nanocrystalline Ni-P electrodeposits provided the basis for i) extensive research programs [e.g. see ref. 10 for a recent review] on many other nanocrystalline electrodeposits (such as pure metals [Ni, Cu, Co, Pd, etc], alloys [Ni-Fe, Co-W, Ni-Fe-Cr, etc] and composites [Ni-SiC, Co-B₄C, etc]) and ii) commercialization efforts for such materials in many different application areas [e.g. 11, 12]. The current paper summarizes some of our important findings over the past 20 years with respect to synthesis, structural characterization and properties of nanocrystalline Ni-P electrodeposits.

2. Synthesis and Structure

Table 1 gives the ranges for plating bath compositions and operating conditions used in most of our research. The phosphorus content in the deposit is controlled by the concentration of the phosphorous acid (H_3PO_3) in the bath. Typical curves showing the increase in the wt%P content in the deposits with increasing phosphorous acid are shown in Fig. 1 [13] for current densities of 1, 5 and 10 A/dm², respectively. Essentially lower current densities result in higher P-content in the deposits at constant phosphorous acid concentration.

Table 1 Bath Composition and Plating Conditions for Nanocrystalline Ni-P Electrodeposits



Fig. 1 Effect of phosphorous acid concentration in plating bath on phosphorus content of Ni-P electrodeposits produced at various current densities [adopted from 13]

The most important factor in controlling the grain size of Ni-P deposits is their phosphorus content. For example, Fig. 2 shows the decrease in grain size (as determined from X-ray line broadening measurements) with increasing P-content, again for the same three current densities of 1, 5 and 10 A/dm², respectively [13]. Very small P-concentrations (<2%) are very effective in grain size reduction as indicated by the very steep slope of the curve in Fig. 2. Deposits with P-content in excess of 5-7 wt% are usually amorphous. It should be noted that in Fig. 2, the "grain size" values of less than ~4 nm for the amorphous deposits containing more than 5-7 wt%P are of course meaningless in terms of grain size per se. Nevertheless, their "grain sizes" as determined by X-ray line broadening are included here to show the smooth transition from nanocrystalline to amorphous deposits. It can further be seen from Fig. 2 that current density in direct current

plating of Ni-P electrodeposits has a negligible effect on grain size. The grain sizes obtained for the various current densities essentially all follow the same line, regardless of current density.



Fig. 2 Grain size reduction with increasing P-content [adopted from 13]

Figures 3 and 4 compare the structural differences between nanocrystalline and amorphous electrodeposits. For the nanocrystalline deposit, bright field (Fig. 3a) and dark field (Fig. 3b) transmission electron micrographs show a very uniform equiaxed grain structure.



Fig. 3 Bright field (a), and dark field (b) micrographs, electron diffraction pattern (c), grain size distribution (d) and X-ray diffraction pattern (e) of a Ni-2.5wt%P sample with an as-plated grain size of 6.1 nm



Fig. 4 Bright field (a), electron diffraction (b) and X-ray diffraction (c) of a Ni-15wt%P amorphous eletrodeposit

The narrow grain size distribution derived from such micrographs (Fig. 3d) shows the typical log-normal behavior usually found for equiaxed grain structures. Because of the small grain size, the electron diffraction pattern (Fig. 3c) shows complete diffraction rings of the Ni-structure, while the X-ray diffraction pattern (Fig. 3e) shows considerable line broadening (in comparison to conventional polycrystalline Ni) resulting from the small crystal size. Both the electron and X-ray

diffraction patterns show only rings/lines of the Ni phase with no additional signals from any of the possible Ni-P intermediate compounds which could form under equilibrium conditions (e.g. Ni₃P, Ni₅P₂, Ni₂P, etc) [14]. In other words, Ni-P electrodeposits are supersaturated single phase materials with P atoms randomly distributed on the face-centered cubic nickel lattice.

In contrast, the bright field electron micrograph (Fig. 4a), electron diffraction (Fig. 4b) and X-ray diffraction pattern (Fig. 4c) of an amorphous Ni-P show the typical features observed for other amorphous structures : very broad diffraction rings or lines and a mottled contrast in the electron micrograph.

4. Properties of Ni-P Electrodeposits

3.1 Hardness

When the hardness of nickel-phosphorus electrodeposits is analyzed as a function of phosphorus content, it is observed that it initially increases up to about 2 wt% and then rapidly decreases with further increases in P content. This unusual behavior can be better understood when examining the hardness as a function of the inverse root of the grain size ($d^{-0.5}$) according to the well-known Hall-Petch relationship [15, 16]:

$$H = H_0 + k d^{-0.5}$$
.....(1)

where H_0 is the hardness at very large grain sizes and k is a constant. Fig. 5 shows such Hall-Petch plots for the electrodeposits described in Figs. 1 and 2. Several important observations can be made in this figure. First, for large grain sizes (>10 nm), the hardness obeys the classical Hall-Petch behavior. However, the hardness does not continue to increase for grain sizes less than 10 nm. Instead, further grain size reduction leads to a softening which is known as the inverse Hall-Petch behavior. Many nanocrystalline materials produced by various synthesis techniques show this transition from regular to inverse Hall-Petch at very small grain sizes [e.g. 17]. While the exact reasons for this behavior are still not completely understood, it is generally accepted that with decreasing grain size, there is a transition from the regular dislocation controlled deformation mechanism operating at large grain sizes to other deformation mechanisms such as diffusional creep or grain boundary sliding [17].



Fig. 5 Hall-Petch plot for the Ni-P electrodeposits shown in Fig. 1 [adopted from 13]

It is interesting to note that the hardness curves presented in Fig. 5 show a smooth transition when going from nanocrystalline deposits to amorphous deposits. Palumbo et al. [18] have explained this behavior in terms of a common structural element in materials with very small grain sizes and amorphous materials. This structural element is the disclination which is introduced into nanocrystals with very small grain sizes in large concentrations through the triple lines separating three adjacent grains. Disclinations have also been used to describe the plastic deformation of amorphous metals.

3.2 Young's modulus

For a series of nanocrystalline Ni-P deposits with relatively constant P-content (~2.5 wt%) and grain sizes varying from about 30 nm to 4 nm, Zhou et al. [19] have recently shown that the Young's modulus, E, begins to decrease when the grain size is less than 20 nm. Fig. 6 shows this decrease expressed as E/E_0 , where E_0 is the Young's modulus of a conventional polycrystalline Ni material. This behavior was explained in terms of the increased interatomic distances between atoms located at the grain boundaries separating differently oriented crystals in the material. For very small grain sizes (i.e. < 20 nm) the volume fraction of atoms associated with grain boundaries increases rapidly resulting in measurable reductions in the Young's modulus. The work by Zhou et

al. also showed that with decreasing grain size the Young's modulus seems to decreases towards the value of an amorphous Ni-P alloy with about 15 wt% P, again suggesting a smooth transition in this particular property when going from nanocrystalline to the amorphous structure.



Fig. 6 Normalized Young's modulus, E/E_{θ} , as a function of grain size for nanocrystalline Ni-2.5wt%P samples, as well as amorphous Ni-15wt%P and pure Ni samples [adopted from 19]

3.3 Taber Wear Index

Jeong et al. [20] studied the relationship between hardness and Taber wear index (CS 17 wheels) for as-plated nanocrystalline Ni-P with grain sizes between 13 nm and 7 nm and phosphorus contents from 0.5 wt% to 2.5 wt%, respectively. The results of this study are summarized in Fig. 7 and show clearly the inverse relationship between hardness and Taber wear index (TWI) as expected from Archard's law [21]. It is interesting to note that the transition from regular to inverse Hall-Petch behavior in hardness is also reflected in the Taber wear index.



Fig. 7 Hardness and Taber wear index (TWI) as a function of grain size of as-plated Ni-P coatings [adopted from 20]

3.4 Corrosion Properties

To date only a few studies have addressed the corrosion properties of nanocrystalline Ni-P. In a study comparing the corrosion behavior during potentiodynamic polarization in $0.1M H_2SO_4$ of nanocrystalline (grain size: 22.6 nm [1.4 wt%P] and 8.4 nm [1.9 wt%P]) and amorphous Ni-P (6.2 wt%P), it was found that neither nanocrystalline nor amorphous Ni-P exhibited significant passivation behavior [22]. This was later attributed to the enrichment of elemental P during preferential Ni dissolution of both materials [23]. X-ray photoelectron spectroscopy of the corrosion films showed that these films are non-protective because the defective surfaces of the nanocrystalline and amorphous surfaces facilitate dissolution and oxidation of surface P atoms from hypophosphite to soluble phosphate anions. Only at very high applied potentials, a thick porous films formed on the nanocrystalline samples which provided a small kinetic barrier to further dissolution resulting in slightly lowered anodic dissolution current densities compared with amorphous Ni-P.

Extensive corrosion testing was done on one particular nanocrystalline Ni-P alloy in conjunction with the development of the first large scale industrial application of nanomaterials in the world [24]. This was the in-situ nuclear steam generator repair technology developed for Canadian and US nuclear reactors in the early 1990's. This repair technology was based on a relatively thick (~1 mm) nickel-phosphorus microalloy (grain size: 80-100 nm, P content: 1500-3000 ppm) applied by electrodeposition on the inside of degraded steam generator tubing to

restore a complete pressure boundary. Various corrosion tests were performed in conjunction with the electrosleeve development including ASTM G28 (susceptibility to intergranular attack), ASTM G48 (susceptibility to pitting and crevice corrosion) and ASTM G35, G36, G44 (susceptibility to stress corrosion, cracking in polythionic acids, magnesium chloride and alternate immersion in sodium chloride, respectively). Tests results showed that the Ni-P alloy was intrinsically resistant to intergranular degradation processes such as intergranular attack and intergranular stress corrosion cracking. Furthermore the material was found to be resistant to pitting and only slightly susceptible to crevice corrosion. It also showed excellent resistance to alkaline environments and reducing acid solutions.

3.5 Thermal Stability

One of the concerns with all nanocrystalline materials is their thermal stability. As a result of their large volume fractions of grain boundaries and triple junctions, there is a large driving force for grain growth at elevated temperatures. Several studies [24-28] have shown that nanocrystalline Ni-P alloys are thermally stable for extended periods of time up to 350 °C. This remarkable stability is a direct result of the large activation energy for grain growth (e.g. 2.25 eV for Ni-1.9wt%P compared to 1.4 eV for nanocrystalline pure Ni [27]) due to very effective grain boundary pinning by P solute and Ni₃P precipitates, which form during the early stages of annealing.

3.6 Magnetic Properties

Fig. 8 shows the effect of phosphorus on the saturation magnetization of Ni-P electrodeposits [29]. All nanocrystalline Ni-P deposits are ferromagnetic, while the amorphous deposits show paramagnetic behavior. Recent spin polarized linear muffin-tin orbital (LMTO) atomic sphere approximation (ASA) calculations have shown that this behavior is mainly determined by alloy composition [30]. The presence of large volume fractions of grain boundaries and triple junctions has little effect on the saturation magnetization in these materials or other pure nanocrystalline metals such as nanocrystalline Ni and Co electrodeposits [31].



Fig. 8 Effect of P content on saturation magnetization for nanocrystalline and amorphous Ni-P alloys [adopted from 31]

5. Ni-P Electrodeposits are Heat-treatable

Nanocrystalline nickel-phosphorus electrodeposits are heat-treatable in the sense that considerable property changes can be induced by phase transformations upon heat treatment. For example, Fig. 9 shows the effect of annealing time on the hardness of nanocrystalline Ni-1.9wt%P with a grain size of 7 nm [32].



Fig. 9 Effect of annealing time and temperature on hardness of Ni-1.9wt%P with a starting grain size of 7 nm [adopted from 32]

At 500 °C and 600 °C, the hardness decreases rapidly with increasing annealing time. However, at 400 °C, the hardness initially increases from about 700 for the as-plated material to over 1200 after 15 minutes of annealing. Further annealing then results in a drop in the hardness back to about the original value after 120 minutes. Detailed electron microscopy studies have shown [e.g. 25, 26] that the initial hardness increase at 400 °C can be attributed to precipitation hardening as a result of the formation of Ni₃P precipitates in the nickel matrix, very similar to precipitation hardening in conventional materials. Particle coarsening and some growth of the nickel grains for longer annealing times result in softening similar to what is observed during overaging of conventional two-phase alloys. At higher temperatures (e.g. 500 °C, 600 °C), precipitation formation and coarsening, and grain growth of the Ni matrix occur so rapidly that the hardness begins to decrease already after very short annealing times.

Jeong et al. [20, 33, 34] have recently demonstrated the beneficial effect of heat treating Ni-P electrodeposits on their Taber wear index as shown in Fig. 10 a and b. For nanocrystalline deposits with P content ranging from 0.5-2.5 wt% (grain size range : 13-7 nm), the hardness values after heat treating were increased considerably over their hardness in the as-plated state (Fig. 10a). This resulted in significant improvement in their abrasive wear resistance as indicated by the reduction of their Taber wear index after heat treating (Fig. 10b).



Fig. 10 Hardness (a) and Taber wear index (TWI) (b) as a function of P content for as-plated and annealed Ni-P coatings[adopted from 20]

6. Conclusions

Extensive research over the past twenty years of nanocrystalline Ni-P alloys produced by electrodeposition has shown that the grain size is strongly controlled by the phosphorus content in

the deposit, which in turn is controlled by the phosphorous acid concentration in the plating bath. The grain size was found to have strong effects on the hardness and abrasive wear resistance of the materials. The hardness as a function of grain size exhibits a transition from regular to inverse Hall-Petch behavior at a grain size of around 10 nm. The Young's modulus is only affected by grain size for deposits with grain sizes less than 20 nm. Grain size has little effect on corrosion properties and saturation magnetization. Rather, these properties are more controlled by the phosphorus content in the deposits. Nanocrystalline Ni-P alloys are heat-treatable allowing for further enhancement of certain properties through a precipitation hardening mechanism.

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8. References

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