The Corrosion Behaviour of Nanocrystalline Electrodeposits

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Nanocrystalline electrodeposits show tremendous improvements in many physical and mechanical properties compared to their conventional polycrystalline counterparts. Of particular concern for their applications as corrosion and wear resistant coatings is their intrinsic resistance to corrosive environments. This paper reviews recent advances in the understanding of the corrosion properties for several nanostructured pure metals (e.g., Ni and Co), alloys (e.g., Ni-P, Co-Ni-Fe) and composites (e.g., Ni-SiC). It will be shown that in many of these materials, grain size reduction to the nanometer range results in considerable improvements in their resistance to localized corrosion such as pitting, intergranular attack and intergranular stress corrosion cracking.

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I. Introduction

In conventional polycrystalline materials, grain boundaries are often prone to intergranular corrosion and stress corrosion cracking because of i) their enhanced energy relative to a defect-free single crystal and ii) differences in chemical composition as a result of solute segregation and second phase precipitates. Therefore, when nanocrystalline materials were first introduced about 20 years ago¹, their corrosion behaviour was initially of great concern as these materials contain large volume fractions of intercrystalline defects such as grain boundaries and triple junctions. The early expectation was that these materials would exhibit very poor corrosion properties. However, detailed studies over the past decade have shown that, for a wide range of electrochemical conditions, grain size reduction in nanocrystalline materials can have a beneficial effect on the corrosion behaviour by providing a microstructure which is highly resistant to localized attack. The aim of this paper is to review some of the key literature on the corrosion behaviour of nanocrystalline metals, alloys and composites prepared by electrodeposition.

II. Nanocrystalline Metals

II-1. Nanocrystalline Ni

Rofagha et al.^{2,3} first investigated the corrosion behaviour of nanocrystalline Ni electrodeposits in an acidic medium (deaerated 2 N H₂SO₄, pH = 0) using potentiodynamic and potentiostatic polarization tests. The results can be summarized as follows. Nanocrystalline Ni electrodeposites (grain sizes of 500, 50, 32 nm, respectively) exhibited similar active, passive and transpassive behaviour as conventional polycrystalline Ni (grain size: 100 μ m), however with about one order of magnitude higher passive current densities (i_p). Using X-ray photoelectron spectroscopy⁴, it was determined that the higher i_p was due to a more defective passive film formed on the highly disordered nanocrystalline Ni surfaces. Another notable observation was the positive shift in the corrosion potential for the nanocrystalline samples which was thought to be the result of the catalysis of the hydrogen evolution reaction. Despite the somewhat enhanced corrosion rate, it was emphasized in these studies that a more uniform corrosion morphology was observed for the nanocrystalline Ni samples.

In an attempt to study in detail the localized corrosion resistance of nanostructured materials, Kim et al.⁵ investigated the effect of grain size and solute segregation on the corrosion behaviour of poly and nanocrystalline Ni containing S impurities (~1000 ppm by weight) in 0.25 M Na₂SO₄ (pH = 6.5). Although the potentiodynamic polarization curves of Ni containing S showed a similar electrochemical behaviour regardless of microstructure (i.e., poly or nanocrystalline), both surface and cross-sectional examination of the corrosion morphologies revealed that nanocrystalline Ni electrodeposits (grain size: 20~30 nm) develop a uniform corrosion morphology exhibiting a high density of evenly distributed shallow pits (<2 µm deep) on the surface. In contrast, the annealed polycrystalline counterpart with a grain size of ~100 µm, suffered considerable localized corrosion, especially along grain boundaries and triple junctions where enrichment of S would be expected after the heat treatment. The tremendous increase in the localized corrosion resistance observed for the nanocrystalline Ni electrodeposits, even at

such a high S content, was interpreted in terms of "solute dilution by grain size refinement", a mechanism originally proposed by Palumbo and Erb^6 . Fig. 1 shows a comparison of the corrosion morphologies for both materials in cross-sectional and planar view.

The good corrosion resistance of nanocrystalline Ni was also observed when the material was exposed to a salt spray environment (ASTM B-117). In this study⁷, both nanocrystalline and conventional Ni electroplated as coatings (thickness: 10 μ m) onto mild-steel substrates were compared. It was shown that nanocrystalline Ni provided the same protection against corrosion of the steel substrate as conventional polycrystalline electrodeposits.



Fig. 1: Scanning electron micrographs showing surface (top) and cross-sectional (bottom) corrosion morphologies of Ni containing ~1000 ppm S. Left) polycrystalline. Right) nanocrystalline⁵.

Tang et al.⁸ compared the corrosion performance of nanocrystalline Ni electrodeposits (grain size: $5\sim10$ nm) prepared using various plating methods (i.e., direct current plating, pulse current and pulse reverse current plating) by immersing test coupons in various acids (7 M nitric, 3 M hydrochloric and 20 g dm⁻³ citric solutions) as well as exposure to moist SO₂ environment. Considerable differences in the corrosion resistance were found among the differently synthesized specimens and the results were interpreted in terms of distinct changes in crystallographic texture observed in these materials.

II-2. Nanocrystalline Co

As a result of their excellent mechanical^{ρ ,10} and wear¹¹ properties, nanocrystalline Co and Co alloys have been recognized as potential candidates for hard chromium replacement coatings. In a recent study, the corrosion behaviour of nanocrystalline Co electrodeposits (grain size: 13 nm) was studied in two environments: i) 0.25 M Na₂SO₄ (pH = 7) and ii) 0.1 M NaOH (pH = 13) solutions^{12, 13}. For 0.25 M Na₂SO₄ solution in which Co does not show passivation, the overall shape of the potentiodynamic polarization curves for both poly and nanocrystalline Co were found to be almost identical and the metal dissolution rate in the absence of a passive film was only slightly enhanced for nanocrystalline Co. However, consistent with the previous results obtained for Ni, the nanocrystalline Co electrodeposits showed higher resistance to intergranular corrosion especially in the presence of impurity elements such as S¹². For the 0.1 M NaOH alkaline solution in which conventional Co readily forms passive films, potentiodynamic polarization tests have shown that the passivation characteristics are not affected by reducing grain size from 10 µm to 13 nm (see Fig. 2).

III. Nanocrystalline Alloys

III.1 Nanocrystalline Ni-P

In the early 1990's, an electrodeposited nanocrystalline Ni microalloy containing P (<3000 ppm by weight) with an average grain size of ~100 nm was developed as a sleeve material for insitu repair of nuclear reactor steam generator tubing which were compromised by intergranular corrosion and stress corrosion cracking^{14,15}. Various corrosion tests (ASTM G28 – susceptibility to intergranular attack; ASTM G35, G36 and G44 – susceptibility to stress corrosion cracking) have shown that the material is intrinsically resistant to intergranular attack and intergranular stress corrosion cracking. The material was also found to be resistant to pitting attack and only slightly susceptible to crevice corrosion.

In another study¹⁶, it was shown that corrosion behaviour of nanocrystalline Ni-P with higher P contents (1.4 wt% and 1.9 wt%) in 0.1 M H_2SO_4 (pH = 0) approaches that of amorphous Ni-6.2 wt% P electrodeposits.



Fig. 2: Potentiodynamic polarization curves obtained in deaerated 0.1 M NaOH (pH = 13) at 298 K (scan rate = 0.2 mV/sec¹³).

III.2. Nanocrystalline Co-Ni-Fe

Electrodeposited Co-Ni-Fe films reportedly possess excellent soft magnetic properties (i.e., high saturation flux density and low coercivity) for potential use in high-density magnetic recording^{17,18}. In a recent study, the corrosion properties of nanocrystalline $Co_{65}Ni_{12}Fe_{23}$ electrodeposits (grain size: 10 ~ 40 nm) in deaerated 2.5 wt% NaCl solution was investigated by Saito et al¹⁹. For the films electrodeposited from a saccharin-free bath at high current density, potentiodynamic polarization curves showed passivation currents of ~30 µm/cm² and pitting potentials of ~0 mV_{SCE}. Although a comparison to the corrosion performance of conventional polycrystalline counterparts of this alloy was not given in this study, these values are comparable to the values typically found for conventional polycrystalline Ni in a similar environment^{20,21}, indicating that the corrosion resistance of Co-Ni-Fe alloys is not compromised by a grain size reduction to the nanocrystalline state.

IV. Nanocrystalline Composites

IV.1. Nano-structured Ni-SiC composites

A comparative wear corrosion study of pure polycrystalline Ni and Ni-SiC nanocomposite coatings using sliding type wear testing and electrochemical impedance spectroscopy in 0.5 M Na₂SO₄ neutral solution was recently reported by Benea et al.²² Compared to the corrosion rate obtained from pure Ni electrodeposits (grain size: >1 μ m), the nanostructured nickel composite (grain size: ~100 nm) which contained nano-sized SiC particles showed a higher polarization resistance and a 50% reduced corrosion rate, already in the absence of wear action. Even higher differences in the material removal rates between the two samples were found when the material was subjected to wear corrosion conditions (e.g., ~90 % reduction at a normal load of 30 N).

V. Conclusions

Contrary to earlier expectations, the corrosion behaviour of nanocrystalline metals, alloys and composites is not compromised by high density of intercrystalline defects (grain boundaries and triple junctions) present in their microstructures. The delocalized corrosion observed in these materials is of significant technological importance for applications in which localized corrosion of conventional materials can result in catastrophic failures. The relatively uniform corrosion observed in nanocrystalline materials is also of importance in lifetime assessment considerations of components for specific industrial applications.

VI. References

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