

The Corrosion Behavior Of Nanocrystalline Electrodeposits

by S.H. Kim, U. Erb,* & K.T. Aust, F. Gonzalez & G. Palumbo

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 improvement in their resistance to localized corrosion such as pitting, intergranular attack and intergranular stress corrosion cracking.

In conventional polycrystalline materials, grain boundaries are often prone to intergranular corrosion and stress

corrosion cracking because of (a) their enhanced energy relative to a defect-free single crystal and (b) differences in chemical composition as a result of solute segregation and second phase precipitates. Therefore, when nanocrystalline materials were first introduced about 20 years ago,¹ their corrosion behavior 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 behavior 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 behavior of nanocrystalline metals, alloys and composites prepared by electrodeposition.

Nanocrystalline Metals

Nanocrystalline Nickel

Rofagha, *et al.*^{2,3} first investigated the corrosion behavior of nanocrystalline nickel electrodeposits in an acidic medium (deaerated 2N H₂SO₄, pH = 0) using potentiodynamic and potentiostatic polarization tests. The results can be summarized as follows. Nanocrystalline nickel electrodeposits (grain sizes of 500, 50 and 32 nm, respectively) exhibited similar active, passive and transpassive behavior as conventional polycrystalline nickel (grain size, 100 μ m), however with about one order of magnitude higher passive current densities (i_p). Using X-ray photoelectron spectroscopy,⁴ it was determined that the higher i_p was due to a more defective passive film formed on the highly disordered nanocrystalline nickel 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 nickel 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 behavior of poly- and nanocrystalline nickel con-

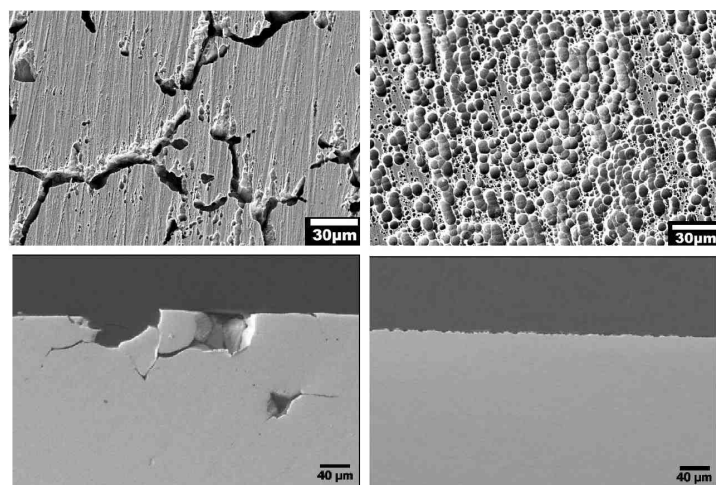


Fig. 1—Scanning electron micrographs showing surface (top) and cross-sectional (bottom) corrosion morphologies of nickel containing ~1000 ppm sulfur. (left) polycrystalline; (right) nanocrystalline.⁵

Nuts & Bolts: What This Paper Means to You

Nanocrystalline electrodeposits show tremendous improvements in many physical and mechanical properties when compared to their conventional counterparts, especially in terms of wear and other physical properties. But what about corrosion? The metallurgist will tell you that there is a lot of active material in there, which would, at first glance, imply poor corrosion resistance. The authors report that the research to date shows the opposite to be true, and discuss their findings here.

* Corresponding Author:
S. Kim c/o Prof. U. Erb
Dept. of Materials Science and Engineering
University of Toronto
Toronto, Ontario M5S 3E4 Canada
E-mail: erb@ecf.utoronto.ca

taining sulfur impurities (~1000 ppm by weight) in 0.25M Na₂SO₄ (pH = 6.5). Although the potentiodynamic polarization curves of nickel containing sulfur showed a similar electrochemical behavior regardless of microstructure (*i.e.*, poly- or nanocrystalline), both surface and cross-sectional examination of the corrosion morphologies revealed that nanocrystalline nickel electrodeposits (grain size: 20 to 30 nm) develop a uniform corrosion morphology exhibiting a high density of evenly distributed shallow pits (<2 μ m deep) on the surface. In contrast, the annealed polycrystalline counterpart with a grain size of ~100 μ m, suffered considerable localized corrosion, especially along grain boundaries and triple junctions where enrichment of sulfur would be expected after the heat treatment. The tremendous increase in the localized corrosion resistance observed for the nanocrystalline nickel electrodeposits, even at such a high sulfur content, was interpreted in terms of "solute dilution by grain size refinement," a mechanism originally proposed by Palumbo and Erb.⁶ Figure 1 shows a comparison of the corrosion morphologies for both materials in cross-sectional and planar view.

The good corrosion resistance of nanocrystalline nickel was also observed when the material was exposed to a salt spray environment (ASTM B-117). In this study,⁷ both nanocrystalline and conventional nickel electrodeposited as coatings (thickness, 10 μ m) onto mild-steel substrates were compared. It was shown that nanocrystalline nickel provided the same protection against corrosion of the steel substrate as conventional polycrystalline electrodeposits.

Tang, *et al.*⁸ compared the corrosion performance of nanocrystalline nickel electrodeposits (grain size, 5 to 10 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 (7M nitric, 3M hydrochloric and 20 g/dm³ 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.

Nanocrystalline Cobalt

As a result of their excellent mechanical^{9,10} and wear¹¹ properties, nanocrystalline cobalt and cobalt alloys have been recognized as potential candidates for hard chromium replacement coatings. In a recent study, the corrosion behavior of nanocrystalline cobalt electrodeposits (grain size, 13 nm) was studied in two environments: (a) 0.25M Na₂SO₄ (pH = 7) and (b) 0.1M NaOH (pH = 13) solutions.^{12,13} For the 0.25M Na₂SO₄ solution in which cobalt does not show passivation, the overall shape of the potentiodynamic polarization curves for both poly- and nanocrystalline cobalt were found to be almost identical and the metal dissolution rate in the absence of a passive film was only slightly enhanced for nanocrystalline cobalt. However, consistent with the previous results obtained for nickel, the nanocrystalline cobalt electrodeposits showed higher resistance to intergranular corrosion, especially in the presence of impurity elements such as sulfur.¹² For the 0.1M NaOH alkaline solution, in which conventional cobalt readily forms passive films, potentiodynamic polarization tests have shown that the passivation characteristics are not affected by reducing grain size from 10 μ m to 13 nm (Fig. 2).

Nanocrystalline Alloys

Nanocrystalline (nickel-phosphorus) Ni-P

In the early 1990s, an electrodeposited nanocrystalline nickel microalloy containing phosphorus (<3000 ppm by weight) with an average grain size of ~100 nm was developed as a sleeve material for *in situ* repair of nuclear reactor steam generator tubing which

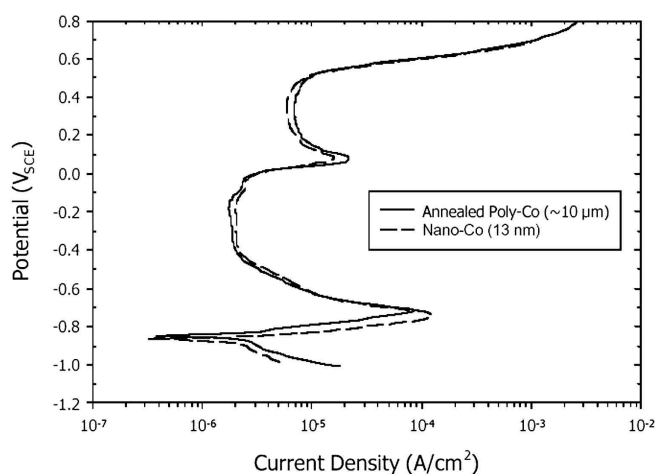


Fig. 2—Potentiodynamic polarization curves obtained in deaerated 0.1M NaOH (pH = 13) at 298°K (scan rate = 0.2 mV/sec.¹³)

was 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 study,¹⁶ it was shown that corrosion behavior of nanocrystalline Ni-P with higher phosphorus contents (1.4 wt% and 1.9 wt%) in 0.1M H₂SO₄ (pH = 0) approaches that of amorphous Ni-6.2 wt% P electrodeposits.

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 Co₆₅Ni₁₂Fe₂₃ electrodeposits (grain size, 10 to 40 nm) in deaerated 2.5 wt% NaCl solution was investigated by Saito, *et al.*¹⁹ For the films electrodeposited from a saccharin-free bath at high current density, potentiodynamic polarization curves showed passivation currents of ~30 μ A/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 nickel 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.

Nanocrystalline composites

Nano-structured Ni-SiC Composites

A comparative wear corrosion study of pure polycrystalline nickel and Ni-SiC nanocomposite coatings using sliding type wear testing and electrochemical impedance spectroscopy in 0.5M Na₂SO₄ neutral solution was recently reported by Benea, *et al.*²² Compared to the corrosion rate obtained from pure nickel 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).

Conclusions

Contrary to earlier expectations, the corrosion behavior 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.

References

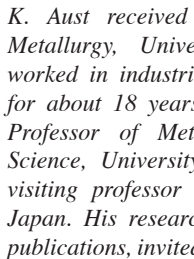
1. H. Gleiter, Proc. 2nd Risø International Symposium on Materials Science, Risø National Laboratory, Roskilde, Denmark, 1981; p. 15.
2. R. Rofagha, R. Langer, A.M. El-Sherik, U. Erb, G. Palumbo & K.T. Aust, *Scripta Metall. et Mater.*, **25**, 2867 (1991).
3. R. Rofagha, R. Langer, A.M. El-Sherik, U. Erb, G. Palumbo & K.T. Aust, *Proc. Mat. Res. Soc. Symp.*, **238**, 751 (1992).
4. R. Rofagha, S.J. Splinter, U. Erb and N.S. McIntyre, *Nanostr. Mat.*, **4**, 69 (1994).
5. S.H. Kim, K.T. Aust, U. Erb & F. Gonzalez, *Proc. AESF SUR/FIN 2002*, AESF, Orlando, FL, 2002; p. 225.
6. G. Palumbo & U. Erb, *MRS Bulletin*, **24**, 27 (November 1999).
7. A.M. El-Sherik & U. Erb, *J. Mater. Sci.*, **30**, 5743 (1995).
8. P.T. Tang, T. Watanabe, J.E.T. Andersen & G. Bech-Nielsen, *J. Appl. Electrochem.*, **25**, 347 (1995).
9. A.A. Karimpoor, U. Erb, K.T. Aust, Z. Wang & P. Palumbo, in "8th International Symposium on Metastable, Mechanically Alloyed and Nanocrystalline Materials" (ISMANAM 2001), *Mat. Sci. Forum*, **386-388**, 415 (2002).
10. J. L. McCrea, G. Palumbo, F. Gonzalez, A. Robertson & K. Panagiotopoulos, *Proc. AESF SUR/FIN 2001*, AESF, Orlando, FL, 2001.
11. G. Palumbo, U. Erb, J.L. McCrea, G.D. Hibbard, I. Brooks, F. Gonzalez & K. Panagiotopoulos, *Proc. AESF SUR/FIN 2002*, AESF, Orlando, FL, 2002.
12. S.H. Kim, K.T. Aust, U. Erb, F. Gonzalez & G. Palumbo, *Scripta Mater.*, **48**, 1379 (2003).
13. S.H. Kim, T. Franken, G. Hibbard, U. Erb, K.T. Aust & G. Palumbo, "9th International Symposium on Metastable, Mechanically Alloyed and Nanocrystalline Materials" (ISMANAM 2002), J.-H. Ahn & Y.-D. Hahn Eds., in the *Journal of Metastable and Nanocrystalline Materials*, **15-16**, 643 (2003).
14. G. Palumbo, F. Gonzalez, A.M. Brennenstuhl, U. Erb, W. Shmayda & P.C. Lichtenberger, *Nanostr. Mat.*, **9**, 737 (1997).
15. F. Gonzalez, A.M. Brennenstuhl, G. Palumbo, U. Erb & P.C. Lichtenberger, *Mat. Sci. Forum*, **225-227**, 831 (1996).
16. R. Rofagha, U. Erb, D. Ostrander, G. Palumbo & K.T. Aust, *Nanostr. Mat.*, **2**, 1 (1993).
17. K. Ohashi, Y. Yasue, M. Saito, K. Yamada, T. Osaka, M. Takai & K. Hayashi, *IEEE Trans. Magn.*, **MAG-34**, 1462 (1998).
18. J.V. Powers & L.T. Romankiw, U.S. patent 4,652,442 (1972).
19. M. Saito, K. Yamada, K. Ohashi, Y. Yasue, Y. Sogawa & T. Osaka, *J. Electrochem. Soc.*, **146**, 2845 (1999).
20. A.I. Asphahani & N. Sridhar, *Corrosion*, **38**, 587 (1982).
21. J. Horvath & H.H. Uhlig, *J. Electrochem. Soc.*, **115**, 791 (1968).
22. L. Benea, P.L. Bonora, A. Borello & S. Martelli, *Wear*, **249**, 995 (2002).

About the Authors

Simon Kim is a PhD candidate in the Department of Materials Science and Engineering at the University of Toronto, Canada. In his research, he is investigating the corrosion properties of various nanocrystalline electrodeposits, including nickel, nickel-phosphorus, nickel-iron-phosphorus, as well as cobalt and several cobalt alloys.



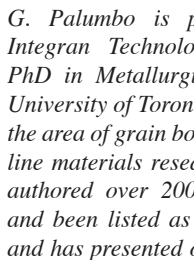
U. Erb and his research group at the University of Toronto is widely recognized as the world leader in the field of electroplated nanostructures. He is the co-author of three patents related to the production of electroplated nanostructures, and has co-authored more than 150 scientific papers in the field of materials science. Dr. Erb holds a PhD in Materials Science from the University of the Saarland, Germany and is currently a Chair in Microengineered Materials at the University of Toronto.



K. Aust received his PhD in Physical Metallurgy, University of Toronto. He worked in industrial research in the USA for about 18 years and then 24 years as Professor of Metallurgy and Materials Science, University of Toronto, including visiting professor in USA, Germany and Japan. His research resulted in over 230 publications, invited lectures in twelve countries, and a dozen major scientific awards, including Fellow of the Royal Society of Canada. Currently, Dr. Aust is Professor Emeritus, working with the Microengineered Materials Group, University of Toronto, and scientific advisor for Integran Technologies.



F. Gonzalez is manager of process and product development at Integran. He received his PhD in Chemical Engineering at the University of Toronto. He has over 22 years combined research and research management experience in the areas of corrosion engineering and electrochemistry applied to the nuclear industry. Dr. Gonzalez is author of numerous reports and papers in these areas. He has also authored three patents.



G. Palumbo is president and CTO of Integran Technologies. He received his PhD in Metallurgical Engineering at the University of Toronto. He has been active in the area of grain boundary and nanocrystalline materials research since 1983. He has authored over 200 scientific publications, and been listed as inventor on 16 patents, and has presented over 30 invited scholarly presentations in this field. Dr. Palumbo serves on the advisory boards of the Center for Materials Research Science and Engineering at Carnegie - Mellon University, and the Metals Technology Laboratory of Natural Resources Canada (CANMET).

