Possible origin of superior corrosion resistance for electrodeposited nanocrystalline Ni

Heather W. Yang [a], I. Roy [b], MingJe Sung [a], F.A. Mohamed [a]*

[a] Department of Chemical Engineering and Materials Science, University of California, Irvine, CA, 92697, USA

[b] Schlumberger, 300 Schlumberger Drive, Sugar Land, TX, 77478, USA

Abstract

We present here for the possible origin of superior corrosion resistance for electrodeposited nanocrystalline Ni and observations that grain boundaries in electrodeposited (ED) nanocrystalline (nc) Ni are predominantly of Σ 3 character. The results are based on orientation imaging microscopy (OIM) performed from electron backscatter diffraction (EBSD). This large volume fraction of coherent low sigma coincidence site lattice (CSL) boundaries appears to be consistent with the superior corrosion resistance of ED nc-Ni in comparison with its coarse-grained counterpart (CGP).

Introduction

Electrodeposited (ED) nanocrystalline (nc) materials have attractive corrosion, mechanical and electrical properties. It has not been made clear why ED nc-Ni, with its large volume fraction of defects in the form of grain boundaries, exhibits superior corrosion resistance than in the case of CGP-Ni . Evidence provided to substantiate these hypotheses or cogent reasons for not observing a higher localized corrosion even in the presence of such a high volume fraction of grain boundaries has not been conclusive. This lack of a possible explanation for the superior corrosion resistance of ED nc-Ni in comparison to CGP-Ni motivated the present investigation. The purpose of this paper is to report some preliminary results obtained in this investigation to shed light on factors that are responsible for enhancing resistance corrosion in nc-Ni.

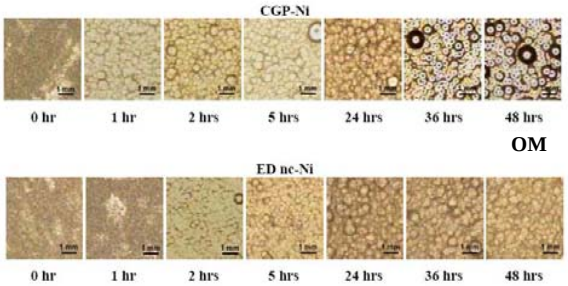
Materials and Experimental Procedure

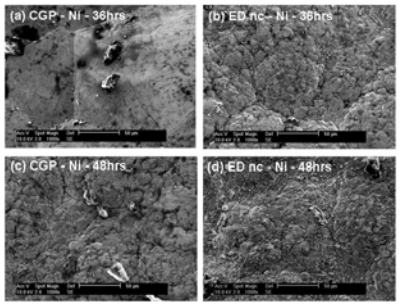
Fully dense bulk ED nc-Ni (99.9%) samples having an average grain size of 100 nm were acquired from Integran Technologies Inc., Toronto, Canada.

The samples were subjected to neutral salt spray tests for different exposure times in a ''Singleton" salt fog chamber for up to 48 hrs. CGP-Ni (99.97% purity) specimens having an average grain size of 40 μm were also subjected to the same environment for the purpose of comparison with ED nc-Ni samples. Salt spray tests were carried out according to ASTM B 117 in a salt fog test system by Singleton at ITT Industries-EC (Cannon), Santa Ana CA. A solution containing 5% sodium chloride with pH at 7 was used in the salt spray tests. The temperature was maintained at 31˚C within the exposure zone of the salt spray chamber. The Optical Micrograph (OM) and Scanning electron micrograph (SEM) were investigated to compare the samples exposure for different period of time.

In an attempt to discern this characteristic, the nature and orientation of boundaries in ED nc-Ni were characterized using electron backscattered diffraction (EBSD). Specifically, this technique was used to generate orientation maps from which assessments of grain boundary coincidence site lattice (CSL) misorientation were obtained. The maps were then produced using Flamenco Channel 5 software (HKL technology) interfaced to a Zeiss Ultra 55 scanning electron microscope.

Corrosion Investigation



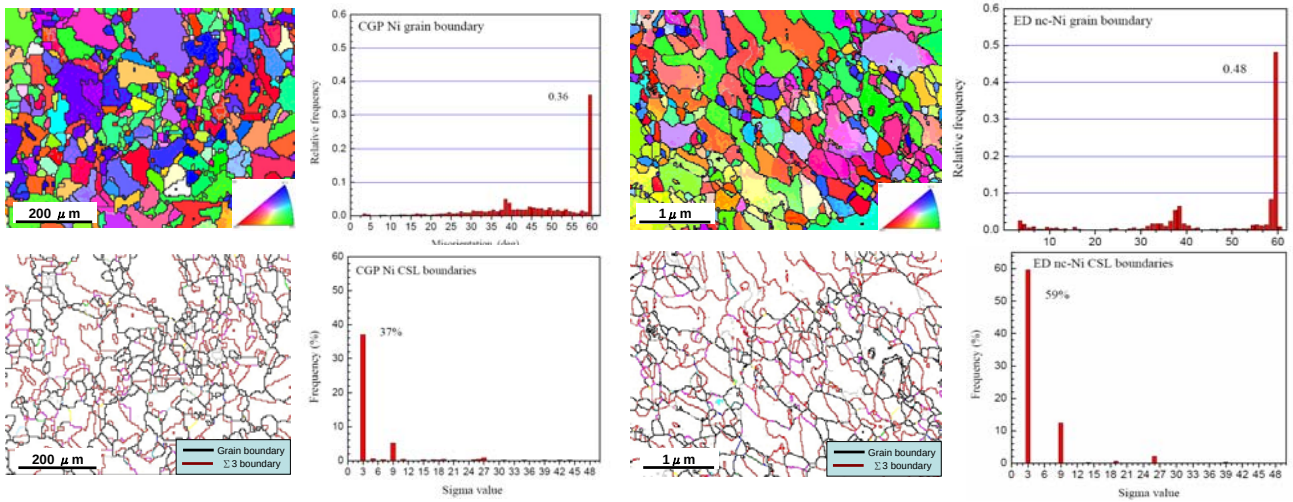


CGP-Ni exposed for (a) 36 hrs and (c) 48 hrs; ED nc-Ni exposed for (b) 36 hrs and (d) 48 hrs.

The resistance of the passive layer on the tested samples increased with exposure time (up to 48 hrs in salt spray chamber) and approximately followed the same trend for both ED nc-Ni and CGP-Ni. This result is indicative of an increase in the thickness of the passive layer for ED nc-Ni as well as its coarse-grained counterpart. In good agreement with experimental observations reported else where, it was noted that the resistance measured across the ED nc-Ni samples was consistently higher than that across the CGP-Ni specimens. This result indicates that superior passivation behavior was responsible for the better corrosion resistance of the ED nc-Ni.

Results

Orientation Image Map and Grain Boundary Analysis



CSL statistics and GB misorientation from OIM of CGP-Ni and ED nc-Ni are shown respectively. Results reveal that the vast majority of grain boundaries present in ED nc-Ni are of high-angle character and approximately 63.8 ± 3% have a preferential orientation within 8.7 ˚ of a 60˚ misorientation on <111 > (Σ 3 boundaries). By contrast, CGP-Ni grains tend to be randomly misoriented with only about 35 ± 2% Σ 3 boundaries present. For the Σ 3 boundaries observed, approximately 90 ± 4% were coherent in ED nc-Ni as compared to about 80 ± 3% in CGP-Ni. The Brandon criteria was employed to distinguish coherent Σ 3 boundaries from incoherent Σ 3 boundaries.

Conclusions

Nanocrystalline materials have a large volume fraction of grain boundaries, many of which are special low sigma CSLs formed during electrodeposition. According to the Σ3 regeneration model, the propensity for Σ3 boundary formation becomes greater as more pre-existing grain boundaries have Σ3 character. We note that this predominance of HAGBs would also favor dislocation accommodated grain boundary sliding during deformation. This accommodation process could prevent or delay the formation of voids at triple junctions during deformation. Thus, ED nc-metals with a large percentage of these special boundaries have great potential for improved salient mechanical properties in addition to excellent corrosion resistance.

In summary, corrosion resistance has been demonstrated to be significantly superior in several ED nc-metals and alloys as compared to their coarse-grained counterparts. Similar observations of enhanced corrosion resistance have been observed in the present work for ED nc-nickel tested under salt spray conditions. The susceptibility to localized corrosion was also found to be lower for ED nc-Ni. These attributes of superior corrosion resistance of ED nc-Ni can be ascribed to the large volume fraction of naturally occurring coherent low sigma CSL boundaries.

Reference

[1] J. H. Qiu, Mater. Sci. Forum 437–438 (2003) 211 .
[2] S. H. Kim, K. T. Aust, U. Erb, F. Gonzalez, G. Palumbo, Scripta Mater. 48 (2003) 1379.
[3] B. N. Popov, Plat. Surf. Finish. 91 (2004) 40.
[4] C. Gu, J. Lian, J. He, Z.H. Jiang, Q. Jiang, Surf. Coat. Technol. 200 (2006) 5413.
[5] R. Mishra, R. Balasubramaniam, Corros. Sci. 46 (2004) 3019.

Acknowledgement

This work was supported by US National Science Foundation (Grant No. DMR-0702978). The use of Zeiss Ultra 55 SEM interfaced with HKL Flamenco Channel 5 EBSD software in the Zeiss Microscopic facility, Cal-IT2, at UC Irvine is greatly appreciated.