

**ASSESSMENT OF CORROSION BEHAVIOR AND STRESS
CORROSION CRACKING SUSCEPTIBILITY OF NANOCRYSTALLINE
BULK AL-MG-BASED ALLOYS IN CHLORIDE CONTAINING
SOLUTIONS**

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In the last few years, nanocrystalline materials (nanoscale grains are defined as those smaller than 100 nm) have received extensive attention as a result of their unique physical, chemical and mechanical properties, and advancements in nanocrystalline material manufacturing and processing has enabled production of bulk nanoscale structural materials [1]. The properties of these nanocrystalline materials cannot typically be predicted from those observed for their conventional polycrystalline counterparts. This is due to the unique structure of nanocrystalline materials with a large number of grain boundaries, which may represent close to 50% of the total volume of the material. It has also been shown that the structure-property relationship of bulk nanocrystalline materials differs considerably from that observed for thin-films nanocrystalline materials [2,3]. The differences are mainly attributed to microstructural variations including crystallographic texture, porosity, impurities, grain boundary and triple junctions.

From the limited corrosion data available in the literature for nanocrystalline alloys, it is unclear whether or not these materials exhibit better or worse corrosion resistance when compared to their microcrystalline counterparts. Improved corrosion resistance has been reported for nanocrystalline 304 stainless steel films [4], nanocrystalline iron [5], and a nanocrystalline Fe-8wt%Al alloy [6]. Inturi et al. [4] reported superior localized corrosion resistance of sputter deposited nanocrystalline 304 SS in comparison to commercially available 304 stainless steel. The increase in localized corrosion resistance was attributed to the fine grain size and homogeneity of the nanostructured material. The authors suggested that the presence of a large number of uniformly distributed defects in the passive film results in a high degree of distribution of chloride ions on the metal surface. Thus, the chloride concentration at each of the defects of nanocrystalline materials is greatly reduced when compared to coarse-grained materials. The electrochemical behavior of hot-compacted nanocrystalline iron in 0.1 M H₂SO₄ was compared to that of microcrystalline iron [5]. The authors found that nanocrystalline iron exhibited lower an active dissolution current and an extended passive region. Based on XPS data obtained for surface films formed on nanocrystalline Ni-P alloys in sulphuric acid [7], Elkedim et al. [5] attributed the passivation process on nanocrystalline iron to the considerable volume fraction of grain boundaries and triple junction present in the nanocrystalline material. They deduced that the grain boundaries enhanced the dissociative adsorption of oxygen and hydroxyl species forming a protective film on the surface. Zeiger et al. [6] reported enhanced localized corrosion resistance for a nanocrystalline Fe-8(wt.%)Al alloy when compared to its microcrystalline counterpart. These authors argued that the high density of grain boundaries favored the enrichment of the grain boundaries with Al and this, in turn, led to higher concentration of Al on the electrode surface.

References to decreased corrosion resistance in comparison to their microcrystalline counterpart alloys also have been reported for nanocrystalline alloys. In a study conducted by Mariano et al. [8], the corrosion behavior of a nanocrystalline FeNb alloy was compared to that of its amorphous counter-part alloy. It was found that the nanocrystalline alloy showed lower corrosion resistance, which authors attributed to the more defective structure of the alloy, and to the formation of the α -Fe phase, which exhibited higher corrosion susceptibility in comparison with the amorphous phase. Alvarez et al. [9] studied the anodic behavior of Fe_{73.5}Si_{13.5-x}Al_xNb₅Cu (x=0-2) amorphous, nanocrystalline and crystalline alloys in a chloride-containing solution. The results indicated that the microstructure of the material had a noticeable effect on the polarization behavior. The amorphous alloy, which has a homogeneous chemical composition, can supply Si to build up a silicon-rich film over the entire alloy surface. On the other hand, heterogeneous distribution of Si in nanocrystalline and fully crystalline alloys impeded the development of a stable passive film. Barbucci et al. investigated the corrosion behavior of nanocrystalline Cu-10(wt.%)Ni in a neutral pH, chloride containing solution [10]. They found that the lower corrosion resistance of the nanocrystalline alloy (with respect to microcrystalline Cu-10(wt.%)Ni) was due to a defective, coarse, and lamellar structured passive layer that formed on the nanocrystalline alloy surface. The presence of that passive layer was detected by SEM and the loss of oxide compactiveness was explained by an increased amount of grain boundaries.

In the research presented in this paper, the corrosion behavior of a series of nanocrystalline Al-Mg alloys is investigated and compared with the corrosion behavior of conventional AA 5083. Since these newly developed nanocrystalline alloys possess excellent mechanical properties [1], they are being considered as a possible replacement for AA 5083 in marine applications. In order to understand the influence of alloying, extrusion rate and microstructure on the

corrosion behavior, electrochemical characterization of the alloy was carried out by potentiodynamic polarization experiments in neutral solution with various chloride concentrations, and intergranular corrosion testing. Additionally, the stress corrosion cracking (SCC) behavior of the conventional AA 5083 and the nanocrystalline Al-Mg alloys was studied. The pitting densities, average pit depths and failure initiation time were measured under different loading conditions after alternate immersion in artificial seawater after time intervals of 2 weeks, 1 month, 2 months and 6 months and after atmospheric exposure at time intervals of 2 months, 6 months, 1 year and 2 years. Scanning Electron Microscopy (SEM) was used to analyze the fracture surface of the failed specimen after removal at selected intervals and tensile testing.

Experimental results showed that the nanostructured Al-Mg alloys did not exhibit significantly superior polarization behavior in terms of passive current density or breakdown potential, when compared to microstructured conventional AA 5083. The open circuit potentials for the nanocrystalline alloys were typically lower than that of the conventionally processed alloy, although this feature is most likely a reflection of a high Mg concentration in these alloys rather than smaller grain size. The pits observed on the nano alloys surfaces were smaller but more numerous than those present on the conventional alloy AA5083. Consequently, the fraction of area occupied by pits on nano alloys was about two orders of magnitude smaller than that on the conventional alloy AA5083. SEM observation of corroded surfaces revealed that corrosion attack for both the conventionally processed and the nanocrystalline alloys initiated at inclusions. In the case of the nanostructured materials, these inclusions were smaller and less numerous than those noted on the conventional alloy. Results of ASTM G-67 intergranular corrosion tests revealed that the nanocrystalline alloys were susceptible to intergranular corrosion while the conventional Al 5083 alloy was resistant. The exchange current densities calculated from cathodic polarization curves for the nano alloys were significantly lower than that for the conventional AA5083. The stress corrosion cracking performance after alternate immersion of the nano Al-Mg alloys was significantly better than that of the conventional 5083 alloy. Al-Mg nanocrystalline alloys exhibited yield and tensile strength (for stressed and unstressed conditions) twice as high as those for the conventional AA 5083 alloy.

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