



The Electrochemistry of Intergranular Corrosion and Sensitization in 5XXX Aluminum Alloys

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ABSTRACT

Future ships for the U.S. Navy are being designed with goals of increased speed and range. The use of 5XXX aluminum alloys for hull and structural materials is attractive due to their high strength-to-weight ratio, fabricability, cost, and availability. These alloys have been used routinely for fast ferries and pleasure craft. These ships and craft are significantly smaller than Navy ships and have substantially different operational and maintenance cycles. In addition, their planned service lives are much shorter than those anticipated by the Navy. Thus, demands on the alloy long-term performance have not been particularly high. Sensitization causing intergranular corrosion and cracking can develop in 5XXX alloys via the formation of beta-phase (Mg_2Al_3) at grain boundaries after exposure to temperatures as low as 70 °C. Such sensitization has been observed to occur in service over periods of 10 to 15 years. Currently, the only means of quantitatively assessing the degree of sensitization (DOS) in 5XXX alloys is through the use of a destructive laboratory test, ASTM G-67. This study investigates the use of electrochemical methods for detection of sensitization in 5XXX aluminum alloys. The electrochemical behavior of AA5456 has been measured in order to develop a fundamentally based, robust, nondestructive, quantitative method for DOS in 5XXX aluminum alloys. In addition to providing a basis for the measurement of DOS, these measurements will be used in the modeling of intergranular corrosion and stress-corrosion cracking of 5XXX alloys by providing boundary conditions for scientific models.

INTRODUCTION

5XXX aluminum alloys are commonly used in naval ship structures. These alloys provide high strength-to-weight ratios while maintaining good as-welded strength and excellent corrosion resistance. However, alloys with above 3 wt% magnesium (Mg) are susceptible to thermal instability. At relatively low temperatures ($\sim 70^{\circ}\text{C}$) over long periods of time (10 – 20 years), the Mg diffuses to grain boundary regions. When the local concentration of Mg is high enough, beta (β) phase (Al_3Mg_2) forms in order to lower the stored energy in the material. The β phase is anodic to the matrix of alloy in seawater and this potential difference provides the driving force for dissolution of the β from the grain boundaries causing intergranular corrosion (IGC) [1]. More importantly, when structures with IGC are under tensile stress, intergranular stress corrosion cracking (IGSCC) may occur [2].

The ability to detect β phase in commercial alloys in the field is therefore of great interest in order to find material that may be susceptible to IGC or IGSCC. The current standard for detecting the degree of sensitization (DoS) in these materials is the ASTM G67 Nitric Acid Mass Loss Test [3]. This test uses the differences in kinetics of dissolution between the matrix and β phase in heated, concentrated nitric acid and measures the mass loss of the material after a 24-hour exposure. However, this test is not amenable to field use due to the destructive nature and long exposure time of the test. Other attempts have been made at detecting IGC susceptibility through electrochemical methods, but have yet to provide a viable solution to detection of it in the field [4].

An electrochemical methodology exists for detecting sensitization in stainless steels, ASTM G108 [5]. In stainless steels, chromium carbides (Cr_{23}C_6) precipitate out of the matrix, leaving chromium-depleted regions around the grain boundaries. The chromium-depleted regions then corrode preferentially to the non-depleted regions. This test records the charge passed after a passivation treatment. The charge passed is then used in a DoS calculation based on constant grain boundary width. This methodology cannot be used as a drop-in solution for detection of sensitization in aluminum alloys due to the differences in the fundamental mechanism (Cr_{23}C_6 depletion rather than β formation) and the differences in the passive films of the alloys.

Quantitative measurement of DoS by an in-situ, non-destructive methodology is not straight forward. Detection of intergranular β phase is difficult because of its small size, (on the order of nanometers). This paper discusses a methodology developed to detect DoS in a fundamentally based, robust, nondestructive, quantitative manner.

APPROACH

Material used was AA5456-H116 $\frac{1}{4}$ " plate. The nominal composition of AA5456 is given in Table 1. Plate material was cut into 1" x 1" squares, then solution heat treated and quenched (SHTQ) at 275°C for 10 hours. Several samples were artificially aged at 100°C from 1 to 30 days. Duplicate ASTM G67 samples (2 " x $\frac{1}{4}$ " x plate thickness) were also prepared in the same manner at each heat treatment. ASTM G67 tests were run according to the test specification in 30°C , 70% vol/vol HNO_3 for 24 hours. Sample mass loss was measured at the end of each test.

Table 1 Nominal composition for AA5456.

Component	Al	Cr	Cu	Fe	Mg	Mn	Si	Ti	Zn	Other, each	Other, total
wt %	balance	0.05 – 0.2	Max 0.1	Max 0.4	4.7 – 5.5	0.5 – 1	Max 0.25	Max 0.2	Max 0.25	Max 0.05	Max 0.15

Electrochemical samples were ground to 1200 grit in ethylene glycol in order to limit the dissolution of β phase during preparation. Samples were rinsed in ethanol, then stored in a desiccator until testing. Electrochemical tests were conducted in a quiescent, pH 11 sodium phosphate buffer solution at room temperature. A saturated mercury/mercurous sulfate reference electrode (MSE) was used, and all potentials are referred to it ($MSE = +0.64$ V(NHE)). Samples were immersed in the buffer solution for 30 minutes prior to testing in order to stabilize the open circuit potential. A preconditioning scan was then conducted from $-1.12 V_{MSE}$ to $0.9 V_{MSE}$ to $-0.1 V_{MSE}$ at a rate of 5 mV/s. Following the precondition, the open circuit potential (OCP) was recorded as a function of time. After the tests, surfaces were examined using optical microscopy to ensure crevice corrosion of the sample did not occur during testing.

RESULTS AND DISCUSSION

An example of the results of the precondition scan is seen in Figure 1. The scan remains within the passive region for this alloy. After the precondition scan, the OCP was monitored with respect to time as shown in Figure 2. Three regions of this curve are seen: (1) an initial drop in potential, (2) a plateau region with a secondary drop in potential, and (3) a stabilization region. In region 1, the initial OCPs decrease as a function of DoS and all OCPs fall immediately and approximately at the same rate. In the second region of this curve, the rate of potential drop decreases (plateau region) with respect to the initial rate of decay, then after some time period increases significantly (secondary drop).

The differences in the OCP behavior between DoS levels is most likely due to the higher concentration of β phase. Assuming a constant cathodic reaction, as the area fraction of β phase present increases, the OCP of material with a higher area fraction of β phase should decrease with respect to a material with most of the magnesium in solid solution. Immediately after the precondition, the OCP of material with a high area fraction of β phase (high DoS) is lower than the OCP of material with a lower area fraction of β phase (low DoS), as seen in Figure 2.

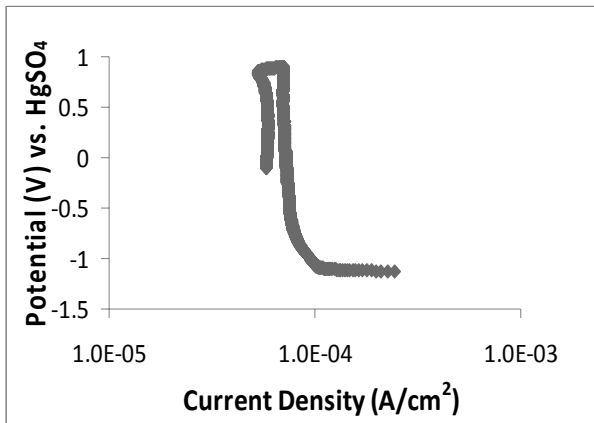


Figure 1 Precondition scan for AA5456.

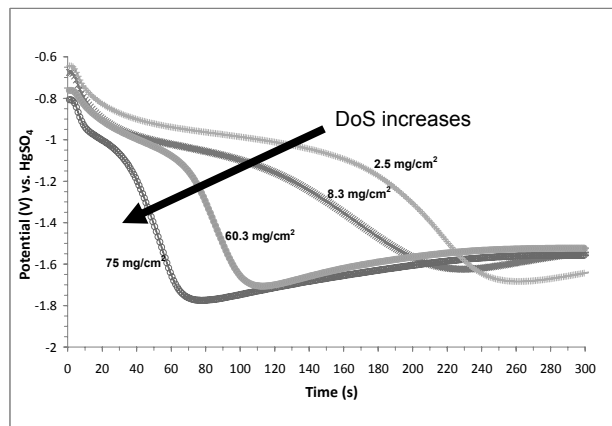


Figure 2 Open circuit decay following precondition scan for AA5456-H116 sensitized to different DoS as determined by ASTM G67.

After 300s, all samples demonstrate equivalent OCPs. The time to reach $-1.2V_{MSE}$ is plotted as a function of DoS for several samples in Figure 3. The largest difference in OCP of sensitized and unsensitized material is seen as potentials drop to approximately $-1.2 V_{MSE}$. A heavily sensitized material (75 mg/cm^2) reaches this threshold potential in approximately half the time of the material that is not heavily sensitized (2.5 mg/cm^2), Figure 3. At this potential, the secondary drop in potential for each sample has commenced and correlates well with the ASTM G67 DoS values. While the function appears to follow a linear trend, the linearity has only been established from DoS levels of $8.3 - 75 \text{ mg/cm}^2$. However, this range is representative of the range seen in the field on Navy ships. The kinetics of the reactions are not yet well understood and continue to be investigated.

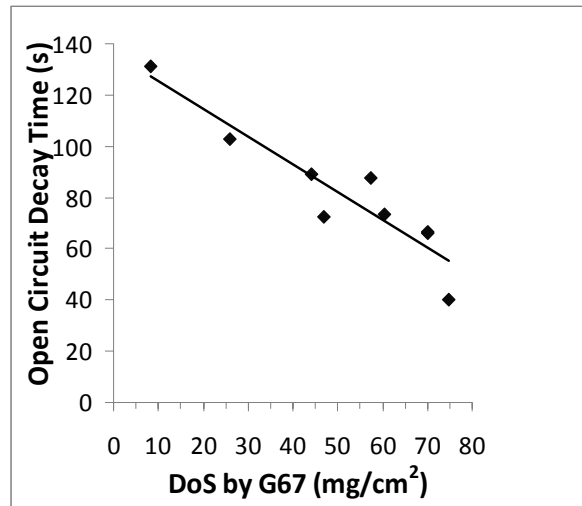


Figure 3 Time for the open circuit potential of AA5456 to drop to $-1.2 V_{MSE}$ as a function of degree of sensitization as determined by ASTM G67.

CONCLUSIONS

A methodology for sensitization detection on AA5456 has been developed. This methodology is based on the open circuit behavior of the alloy after a precondition scan. The initial OCP after preconditioning and the time required for material to reach $-1.2 V_{MSE}$ correlate with the current standard for determining intergranular susceptibility, ASTM G67. This methodology, once validated, could act as a test method for detection of sensitization in the field.

The role of the precondition scan on this alloy is still being investigated. The precondition scan is essential for distinguishing between DoS levels. This precondition step is similar to the passivation step in the potentiokinetic reactivation for stainless steels. However, rather than measuring a rapid decay in current density as in the case of the stainless steel, for 5XXX alloys, a decay in OCP is measured. Using OCP as a distinguishing characteristic may not be an ideal measurement, due to the dependence of OCP on variables such as temperature and dissolved oxygen content. Dissolved oxygen should not play a significant role in the reactions occurring due to the high pH of the electrolyte. The dependence of OCP on temperature, however, should be investigated.

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