MEASURING SENSITIZATION OF AA 5083 USING RESISTIVITY, NONLINEAR ACOUSTICS, AND ATTENUATION

Aaron J. Bailey - April 2011
Materials Science and Engineering Department
University of Virginia, Charlottesville, VA

Because of their high strength-to-weight ratio and resistance to corrosion, 5xxx aluminum alloys are in demand for many marine applications. However, catastrophic failure can occur in 5xxx due to sensitization. This research focuses on evaluating potential nondestructive methods to monitor sensitization in a 5083 aluminum alloy, including resistivity, nonlinearity, and attenuation. The resistivity decreased during the sensitization treatments, and it showed the most reliable trends in monitoring the degree of sensitization. Although the nonlinearity and attenuation measurements show trends with sensitization heat treatment, more work is need to reduce the variability in the measurements in order to better relate their behavior to sensitization.

Introduction

Because of their high strength-to-weight ratio and resistance to corrosion, 5xxx series aluminum alloys are in demand for many marine applications, including the hulls of ships. Magnesium is the main alloying element in these lightweight alloys. These alloys are not heat-treatable; instead they are strengthened by strain hardening.

However, catastrophic failure can occur in 5xxx due to sensitization and stress corrosion cracking. Sensitization results in 5xxx alloys containing more than 3 wt% of Mg when they are exposed elevated temperatures (>50ºC) over a long period of time (ASTM; Bovard, 2005; Oguocha et al., 2008). Mechanistically, the β-phase, Mg2Al3, forms on the grain boundaries, which are the interfaces where crystals of different orientations meet. As the percentage of β-phase precipitates at the grain boundaries increases, the material is said to be sensitizing and as it becomes “sensitive” to stress corrosion cracking (SCC) and intergranular corrosion. Stress corrosion cracking results in brittle failure of a material that is normally ductile. It can occur at even moderate stresses in mildly corrosive environments, such as sea atmosphere and sea water. Thus, although the 5xxx aluminum alloys are very light and durable due to the high magnesium content, sensitization limits their application.

The ASTM G67 is the industry standard that provides a measure of the propensity to sensitization of Al-Mg alloys. The specified process uses nitric acid to dissolve only the precipitated β-phase, i.e. Mg2Al3, and the mass loss is measured. The degree of sensitization (DOS) is the mass of loss per unit surface area of the sample (mg/cm²). DOS increases as the degree of β-phase precipitate continuity increases on the grain boundaries. The material is prone to SCC when the DOS is between 25 to 75 mg/cm², and resistant to SCC when the materials lose less than 15 mg/cm². (ASTM G67, 2004).

In service, sensitization occurs over a long period of time, and it is vital to be able to monitor the sensitization of the alloy during use. Thus a reliable means to nondestructive evaluate (NDE) the sensitization could prevent catastrophic failures from occurring.

Aluminum alloy 5083-H131 is a commonly used marine alloy in high stress applications and was tested in this experiment. In order to nondestructively measure the sensitization of the alloys, it was determined that resistivity, nonlinearity, attenuation are sensitive to the precipitation processes termed sensitization. Past results obtained using ultrasonic nonlinearity and attenuation measurements have not shown a definite trend (Amaro, 2010). Therefore, another method to
analyze the data was needed. Measuring the changes in the resistivity of the sample might help to discriminate between these possible micro-changes since resistivity is directly influenced by solute content (Reaisinia, 2003). The main scope of this study was measuring the resistivity and comparing those results to ultrasonic attenuation and nonlinearity.

During sensitization heat treatments, there are multiple aspects of the material microstructure that might change, such as dislocations and solute, (Cantrell & Yost, 1993), and this can obscure the specific meaning of the results. For example, in the strain-hardened alloys, such as AA 5083-H131, there is a network of dislocations as well as the dissolved atoms of the alloying additions (i.e. solute) that could possibly change during sensitization. However, by having various independent approaches to assess the state of sensitization, the results can be more clearly interpreted.

**What affects the Resistivity of a metal?**

Resistivity is the extent to which a material opposes electrical current. Electrons that carry the current do not flow straight through a material because their path is scattered by dislocations, vacancies, solute atoms, and grain boundaries. The fewer collisions an electron has, the faster it travels and the lower the resistance. In short, the distance between collisions varies inversely with resistivity. Matthiessen’s rule suggests the contributors to resistivity are independent (Ohring, 1995). Thus, their effects on the resistivity are additive. Increasing temperature overwhelmingly increases the scattering and thus resistivity. Therefore, in order to observe changes due to only certain elements, such as dislocations and solute content, measurements need to be made at very low temperatures.

**What causes Nonlinearity?**

Many engineering materials exhibit Hookean elastic behavior described by the relationship, $\sigma = E\varepsilon$, where $\sigma$ is the stress in the material, $\varepsilon$ is the elastic strain, and $E$ is the elastic modulus or material stiffness. (This relationship may also be expressed as $\sigma = A\partial u/\partial x$, where $A$ is a coefficient of second order elastic stiffness tensor expressed in terms of the displacement gradient, $\partial u/\partial x$.)

This linear relationship is derived from the potential energy versus interatomic spacing relationship. If the potential energy well is assumed to be symmetric (dotted green curve) as shown in Figure 1, then the slope (solid green line), which is the elastic modulus $E$, is a linear relationship. However, when the shape of the energy curve is, in general, not symmetric (black curve) and there is a nonlinear slope (red curve).

![Figure 1: Energy Curve (Zhigilei, 2009)](image)

Thermal expansion also results from a nonsymmetrical energy versus interatomic spacing curve, and thus there is a relationship between thermal expansion and the intrinsic lattice anharmonicity of a material.

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1 For clarity, the concepts are introduced in 1-D form; however, complete tensorial details are available in the literature (Hikata, Chick, & Elbaum, 1965)
Additionally nonlinearity arises from the presence of dislocation and precipitates. The nonlinearity is directly affected by dislocations movement and thus indirectly by precipitates (Hikata et al., 1965). In fact, the above intrinsic nonlinearity is small with respect to the defect-induced nonlinearity.

When some materials (or springs, for that matter) exhibit a nonlinear behavior, they may be characterized by the following relationship.

\[
\sigma = A \frac{\partial u}{\partial x} + \frac{1}{2} B \frac{\partial^2 u}{\partial x^2}
\]  

(1)

where B is a coefficient of the third order elastic constants. The level of nonlinearity exhibited by such a material may be defined by a so-called nonlinearity parameter, \( \beta = \frac{B}{A} \).  

(2)

This is an experimentally accessible parameter, and theory suggests that it is sensitive to small changes in material microstructure, which are known to have large impact on material performance (Dace, 1992).

Materials with nonlinear behavior will give rise to second, third, fourth, … order harmonic signals, i.e. waves with frequencies which are 2, 3, 4, … times that of the input signal. For a wave \( u = A \sin(\omega t) \) passing through a nonlinear solid whose behavior is described by (Eq. 1), the wave equation of motion for the first and second harmonics is

\[
\rho \frac{\partial^2 u}{\partial t^2} = A \frac{\partial^2 u}{\partial x^2} + B \frac{\partial u}{\partial x} \frac{\partial^2 u}{\partial x^2}
\]  

(3)

The solution to this governing equation consists of sinusoidal waves with frequency dependent amplitudes, and can be solved iteratively for the nonlinearity parameter \( \beta \)

\[
u(x,t) = A_1 \sin(kx - \omega t)
\]

\[
-\frac{1}{8} \frac{B}{A} (A_1 k)^2 \cos(2(kx - \omega t))
\]

\[
+ \ldots \text{HOT}
\]  

(4)

The amplitude of the second harmonic, \( A_2 \), then is

\[
A_2 = \frac{1}{8} \frac{B}{A} (A_1 k)^2 x
\]  

(5)

Solving for \( \beta \)

\[
\beta = \frac{B}{A} = \frac{8 A_2}{A_1^2 k^2 x}
\]  

(6)

where \( A_1 \) and \( A_2 \) are the amplitudes of the first and second harmonic waves, once they pass through the material; and \( x \) is the sample thickness. The parameter \( k \) is the wave number, (rotational frequency/velocity).

What affects the attenuation?

Attenuation is the damping of a wave as it passes through a medium. The value of attenuation depends on the medium and on the path length of the wave. Some of the attenuation (or mechanical damping) of the wave is frequency dependent, but not all. As a wave passes through the sample, the frequency dependent portion of attenuation is caused by a phase lag due to some damping mechanism. The amount of attenuation increases when the input wave frequency is near the resonant frequency. For example, there is a resonant frequency associated with the loop length of the dislocations. Thus changes in dislocation density and configuration are expected to influence the attenuation. Additionally, the non-frequency dependent attenuation of a wave results from the cyclic nature of the stress passing through the material that causes a hysteresis loop. (Granato & Lucke, 1956).

Attenuation is defined by an attenuation coefficient, \( \alpha \), as shown in equation 7.

\[
\alpha = \frac{\log \frac{V_{\text{input}}}{V_{\text{echo}}}}{x}
\]  

(7)

where \( V_{\text{input}} \) is the input wave, \( V_{\text{echo}} \) is the first echo, and \( x \) is the distance the wave travels in the sample from \( V_{\text{input}} \) in to \( V_{\text{echo}} \).
Experimental Methods

Resistivity:

One method to measure resistivity is to measure the electrical resistance and calculate the resistivity using the following equation,

\[
\rho = \frac{R A}{L}
\]

where \( R \) is the resistance, \( \rho \) is the resistivity, \( L \) the length of the sample between the contacts, and \( A \) the sample as shown in Figure 2.

![Figure 2: Sample](image)

The intrinsic resistivity of pure aluminum is low, on the order of \( 2 \times 10^{-8} \) \( \Omega \) m. Thus, a very sensitive measurement system must be used, such as the four point probe method employed on a long, slender sample, as shown in Figure 3.

![Figure 3: Resistivity measurement setup](image)

One set of wires supplied a current and the other set measured the voltage drop across the sample. The resistance between the voltage probes can be calculated by measuring the current and apply the \( R = \Delta V/I \).

Two different tempers of AA 5083 were tested: the as-received cold-rolled (H131) and the Solution Heat Treated and Quenched (SHTQ). H1 means the alloy was strain hardened without thermal treatment, 3 means, signifies the degree of hardening between O (annealed) and 8 (ultimate strength), and the last digit, 1 signifies little additional strain hardening by shaping of the sample. The SHTQ samples were cut from the same block but were heated to 285ºC for 10 hours, and then quenched rapidly in cold water. To speed up the sensitization process, the samples were artificially aged at 100ºC from 1 to 30 days, and measurements were taken at 0, 7, 14, 30 days.

The sample dimensions chosen were 1/8 in by 1/8 in by 12 inches, and they were cut by an electro-discharge machining (EDM) process. The length was measured with vernier calipers and the area was measured with a micrometer five times along the length of the rod and averaged. Two copper wires (22 AWG) were spot welded on the end of each rod and secured as shown in Figure 2. The resistivity of the samples was measured at liquid nitrogen temperature (77 K) to minimize the temperature affect on the resistivity, and the voltage was measured within 1 microvolt.

Nonlinearity and Attenuation

Ultrasonic nonlinearity and attenuation were measured using material taken from the same plate as the resistivity measurements. Five samples of H131 and SHTQ were cut to approximately 1 in by 0.7 in by 0.5 inch. Samples were polished to be optically flat and parallel within 162 arcseconds (Amaro, 2010).
The five samples of each type were exposed to 100°C for 0, 7, 14, 30 and 60 days, respectively. Nine measurements were made at different locations on each sample.

In order to measure the nonlinearity parameter, $\beta$, an ultrasonic wave generator was used to send a precise single wavelength voltage to a piezoelectric contact transducer that, in turn, sent a compressive sound wave through the probed material as shown in Figure 4.

Another similar transducer on the opposite side of the sample converted the sound wave which has propagated through the material back into an electrical signal that can be recorded by an oscilloscope and analyzed.

The RITEC 5000 SNAP system was used as the voltage pulse generator, and the setup and procedure is described by Dace (1992) and shown in Figure 4. Using this setup, a voltage wave, $V_{\text{in}}$, of single frequency is initiated in the material, as shown in, and the exiting waveform, $V_{\text{out}}$, is measured. The different exiting wave frequencies of $V_{\text{out}}$ may be separated by the Fourier transform (converts the wave from time to frequency domain) as shown in Figure 5 and the inverse FFT is performed on different parts of the frequency spectrum to produce the first and second harmonic waves.

![Figure 4: Primary Setup](image)

![Figure 5: FFT (left) and reconstructed wave after inverse FFT (right)](image)
Using the amplitudes of the first and second harmonic waves, $A_1$ and $A_2$, the nonlinearity parameter $\beta$, of the material, can be determined by Eq. 6. Once the nonlinearity parameter is measured, the microstructure can be examined to determine the correlation between the two as shown by Dace et al. (1992) and Hikata et al. (1965).

Results

Resistivity:

Figures 6-8 show the resistivity of AA 5083 SHTQ and H131 after annealing 0, 7, 14, and 30 days at 100ºC. The general trend for both sample types is a decrease in resistivity, but the H131 has greater resistivity and shows a much greater initial decrease as shown in Table 1 and Figure 7. Since the H131 has more dislocations initially than SHTQ, the greater initial decrease is presumably due to annealing of the dislocations.

Table 1: Average slopes of SHTQ and H131

<table>
<thead>
<tr>
<th></th>
<th>SHTQ</th>
<th>H131</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Average slopes (10^{-11}) $\Omega$ m/day</td>
<td>Average slope (10^{-11}) $\Omega$ m/day</td>
</tr>
<tr>
<td>0-7 Days</td>
<td>-1.38</td>
<td>-7.43</td>
</tr>
<tr>
<td>7-14 Days</td>
<td>-1.85</td>
<td>-1.93</td>
</tr>
<tr>
<td>14-30 Days</td>
<td>-0.91</td>
<td>-1.38</td>
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The repeatability of the measurements was determined by measuring several of the samples 2-3 times each on the same day. The difference between measurements for the same sample were all below 0.5% and most below 0.25%. Additionally, the current direction was also switched to verify no discrepancy.

There are two uncertainties that do not affect the resistivity variation for a given sample during sensitization. First, the uncertainty in the resistance of the resistor used in the circuit affects all measurements equally since the same resistor was used for every measurement, and thus the resistance variation is negligible from measurement to measurement.
Second, the dimensions of the sample (cross sectional area and the length) would only affect the value of resistivity between samples since they are constant for a given sample. This uncertainty in area is, in fact, the main contributor to the overall uncertainty in the measured resistivity between samples. Without these three uncertainties, the uncertainty for a given sample at different days of sensitization is very low. If the uncertainty of the area and length is removed, the uncertainty drops by over 68% from $3.70 \times 10^{-10}$ $\Omega$ m to $1.11 \times 10^{-10}$ $\Omega$ m and the percent error from 1.1% to 0.31%. This is confirmed by the strong similarity in the trends between samples. All the measurements are within 2% of the average and about 80% of the measurements are within 1% of the average.

Additionally, as verification of the absolute value of the measurements, according to the ASTM Metals Handbook (1990) the electrical resistivity of 5083 O at 20ºC is $6.0 \times 10^{-8}$ $\Omega$ m. For this experiment setup, the average resistivity at room temperature in the lab (approx. 20ºC) was $5.97 \times 10^{-8}$ $\Omega$ m. A comparison of the average resistivity between SHTQ and H131 is shown in Figure 8.

Figure 8: Average Resistivity versus Days at 100ºC of AA 5083 H131 and SHTQ

Nonlinearity and Attenuation:

The ultrasonic nonlinearity parameter $\beta$ and attenuation was measured at 0, 7, 14, 30 and 60 days (see Figure 9). Both H131 and SHQT showed an increase in $\beta$ up till 14 days. After 14 days, the H131 tempered material continued increasing and SHTQ started decreasing, or remained flat. Due to the high variability, there is not a conclusive trend for $\beta$ in both samples. However, by applying better methods for measuring $\beta$, experimentation might show better trends if the variability of $\beta$ is reduced.

Figure 9: $\beta$ versus Days at 100ºC of AA 5083 H131 and SHTQ

Attenuation of the 10 MHz initially decreases rapidly in the SHTQ samples. For the H131 samples, the attenuation initially increases and then peaks and levels out as shown in Figure 10. As shown by the resistivity measurements, there is an initial drop in the number of dislocations in the H131 samples, which means the loop length should increase rapidly. Though not shown in the graph, 10 MHz attenuation decreased linearly with DOS as well.

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Figure 10: Attenuation versus Days at 100ºC of AA 5083 SHTQ

Figure 11: Attenuation versus Days at 100ºC of AA 5083 H131

Summary Discussion

Since “days of sensitization” cannot be applied as directly to real life situations, it is more important to plot the data versus the industry standard DOS and %β concentration along the grain boundaries. In Figure 12, the resistivity is plotted against the %β-phase concentration along the grain boundaries of the sample (Lim, M. & Jain, S., 2011). After 47% β on grain boundary (7 days, 24 DOS), the resistivity drops more dramatically, suggesting that resistivity may be more sensitive as β-phase covers about half of the grain boundary.

Figure 13 shows resistivity versus DOS. The correlation between DOS and days at days at 100ºC was done according to the ASTM G67 (Adedeji & Lim, 2011). (Note: The H131 curve is based off the assumption that DOS varies the same with %β-phase covering grain boundaries as the SHTQ samples. But this may not be true since some experimentation has shown that H131 samples exhibit accelerated corrosion rates relative to SHTQ samples (Lim & Jain, 2011).
The final goal of these experiments was to monitor sensitization by a nondestructive method. Resistivity measurements showed an a steady decrease in resistivity as the material sensitized, but sample to sample variation was still greater due to dimensional uncertainty. In order to use resistivity to monitor sensitization, the same test specimen would need to be used throughout the service life. The nonlinearity parameter, $\beta$, showed sensitivity to sensitization as well but definite trends are not clear for both samples and the high variation between measurements poses a considerable problem. Measuring $\beta$ may feasible to monitor sensitization, but improvements in the measurement setup is needed to reduce variation. Attenuation showed it was affected by sensitization but again definite trends for both types of samples could not be established due to high uncertainty. Overall, Resistivity shows the best trends and lowest uncertainty and is a viable means to nondestructive evaluate sensitization of 5xxx aluminum alloys.

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Works Cited


