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## THE EFFECT OF CRYOGENIC TREATMENTS ON PITTING CORROSION SUSCEPTIBILITY OF AA5083-H111 IN 3.5% NaCl ENVIRONMENT

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**Abstract:** Application of aluminium alloys is increasing in all industries due to its combined properties of low weight, good mechanical resistance, thermal conductivity, electrical conductivity, high strength, and good corrosion resistance. In particular, AA5083-H111 alloys have been successfully used in the maritime sector. Unlike purely surface treatments, cryogenic treatment is an inexpensive one-time process that influences the core properties of the components. Cryogenic treatment has recently been introduced to Al alloys. Although the main mechanisms are still ambiguous, considerable improvements on mechanical properties are well noted. However, the effect of cryogenic treatment on the corrosion of Al alloys is limited.

This study investigated the effect of shallow cryogenic treatment (-80 °C) on the corrosion of 5083-H111 aluminium alloy, which is used particularly in the shipbuilding industry. Plates of 6-mm thickness exposed to a 3.5% NaCl environment were evaluated via Brinell hardness measurements, Electrochemical Impedance Spectroscopy (EIS) and surface monitoring methods including atomic force microscopy (AFM) and optical profilometry (OP) applied before and after the effect of cryogenic treatment.

Results indicated that the duration time of cryogenic treatment (24 h, 36 h and 48 h) had little effect on changing the hardness values and corrosion response of AA5083-H111 alloy in the 3.5% NaCl environment.

**Keywords:** AA5083, corrosion, cryogenic, hardness, AFM

### 1. INTRODUCTION

The mechanical properties of aluminium, the most abundant element of the earth's crust, can be improved by alloying it with other metals. Aluminium and its alloys are the most widely produced among the non-ferrous metals due to their lightness, processability, high corrosion resistance, and capability of being recycled. Recently, various methods such as aging, heat treatment and cryogenic treatment have been applied to increase the strength of aluminium alloys and improve their mechanical properties.

The properties of materials show significant improvements with the application of cryogenic treatment in its two forms as deep and shallow cryogenic treatment. Shallow cryogenic treatment is more common and is applied to materials at up to -90 °C. The deep cryogenic process is applied to the material at temperatures below -90 °C [1]. With cryogenic treatment, increases have been determined in the mechanical properties of materials such as yield, tensile strength, fatigue, impact strength, hardness, corrosion resistance [2], ductility, toughness and modulus of elasticity.

The 5083 aluminium-magnesium alloys, which have high corrosion resistance and moderate strength, are widely used in the shipbuilding industry in single- or multiple-hull high-speed ferries, cryogenics, transportation equipment and armor plates [3-5]. Because the environments where the 5083 Al-Mg alloys are used are severe, their properties need to be improved. These alloys are hardened only by cold treatment [6].

An H-designated temper is applied to develop the mechanical properties of the 5083 Al-Mg alloys, which are among those of the 5XXX series with the highest magnesium content. In the H111 temper designation, the first digit after H indicates strain-hardened only, the second digit indicates the degree of strain hardening (1/8 hard) and the last digit indicates the variation of the two-digit temper [7]. The elements of Cr and Mn in the composition of 5083-H111 control the stress corrosion of the alloy and increase its mechanical properties. The 5083-H111 is widely used in automobile production, aerospace parts and machine production [8].

In the present study, cryogenic treatment was applied to 5083 Al-Mg alloy at -80 °C for 24, 36 and 48 h, and Brinell hardness tests were performed. After cryogenic treatment, the corrosion resistance of the metal in a 3.5% NaCl medium was investigated by using Electrochemical Impedance Spectroscopy (EIS). After the corrosion tests, AFM and OP methods were applied to examine surface morphologies

## 2. MATERIALS AND EXPERIMENTAL PROCEDURE

### 2.1 Materials and Chemicals

The studied 5083-H111 aluminium alloy was supplied from ALRO S.A., Romania. The

chemical composition (wt %) of the metal is listed in Table 1. The metal samples for corrosion and surface morphology studies were prepared following the method previously described by the authors. The corrosion environment was prepared using NaCl obtained from Sigma-Aldrich.

### 2.2 Corrosion Measurements

Electrochemical Impedance Spectroscopy (EIS) experiments were done using a Gamry instrument, Reference 600. All the electrochemical corrosion studies were conducted at room temperature using a three-electrode cell in which a Pt plate and Ag/AgCl were used as the counter and reference electrodes, respectively. The working electrodes (i.e., 5083-H111 samples) were embedded in epoxy resin with only 0.785 cm<sup>2</sup> exposed to the corrosive solution (3.5% NaCl). Before EIS measurement, the open circuit potential (OCP) was measured for a 2-h period in order to achieve a steady-state potential. The EIS measurements were carried out in a frequency range of 100 kHz–0.1 Hz with an applied AC signal of 10 mV. The equivalent circuit simulation program (ZSimpwin 3.21) was used for data analysis, the equivalent circuit synthesis and the experimental data fitting. In order to obtain a reproducible result, experiments were repeated seven times under the same conditions and the closest values presented as the result.

### 2.3 Hardness Testing

The DIGIROCK-RB hardness tester (Fig. 1) was used to calculate the Brinell hardness of each sample and the average of seven repeated measurements was taken. A load of 60 kg was applied to determine the hardness of the samples using an 8-mm-diameter ball indenter with a 3-s dwell time.

**Table 1.** Chemical composition of aluminium 5083-H111

	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ni	Ti	Sn	Zr	Al
AA5083-H111	0.075	0.404	0.031	0.276	4.300	0.081	0.012	0.007	0.018	<0.002	<0.005	94.796



Figure 1. Hardness testing equipment

## 2.4 Surface Morphological Screening

After electrochemical measurements for all studied conditions, the AA5083-H111 surface morphologies were examined [9] by means of the AFM (PARKSYSTEMS, Model: XE-100E) and OP (Phaseview, Model: Zeescope) (Fig. 2).

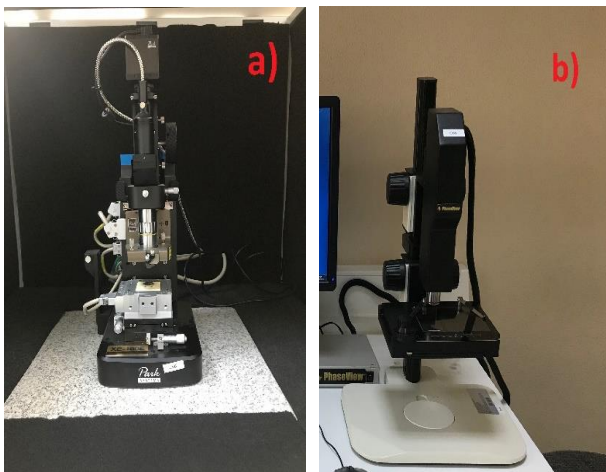


Figure 2. Equipment for AFM (a) and OP (b)

## 3. RESULTS AND DISCUSSION

### 3.1 EIS Measurements

The impedance method provides information about the kinetics of the electrode processes and simultaneously about the surface properties of the investigated systems [10]. Figure 3 presents the EIS results recorded for the AA5083-H111 alloy samples without and with 24, 36 and 48 h shallow cryogenic treatment ( $-80\text{ }^{\circ}\text{C}$ ) exposed to 3.5% NaCl solution. The EIS results are shown in Fig. 3

with (a) Nyquist, (b) Phase angle, and (c) Bode modulus representations. In order to obtain relevant electrochemical parameters, an equivalent circuit diagram, as shown in Fig. 4, was selected for fitting the obtained impedance results. The goodness-of-fit parameter (variance,  $\sigma^2$ ) for all selected experimental data was not greater than  $2.1 \times 10^{-3}$ .

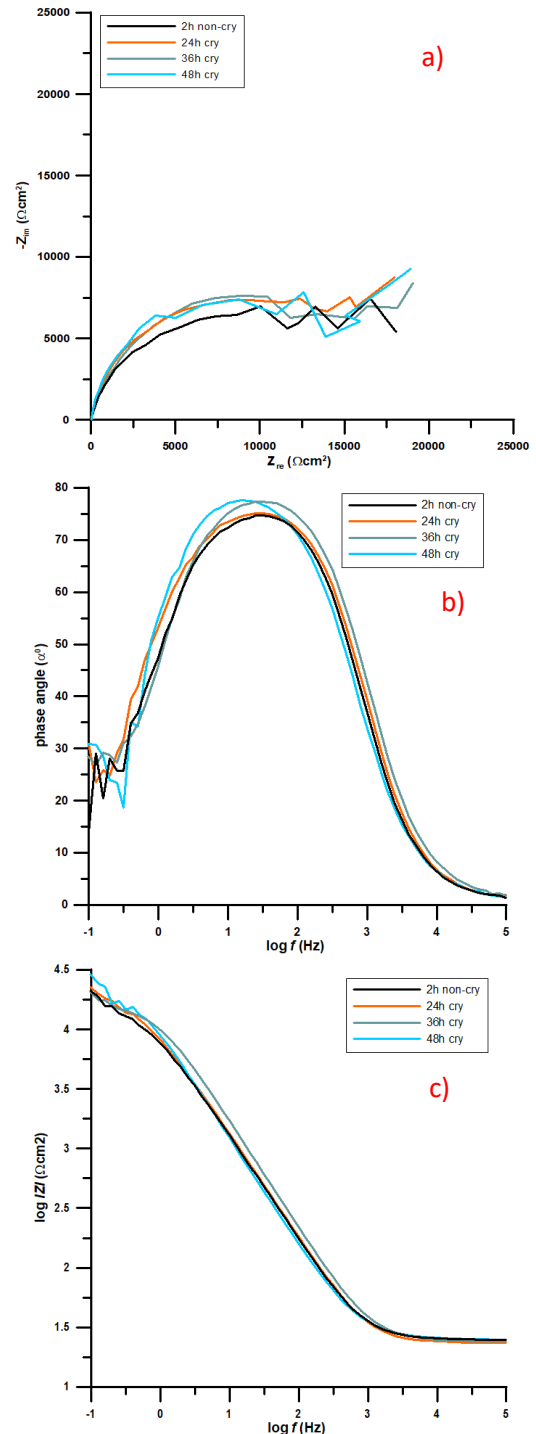
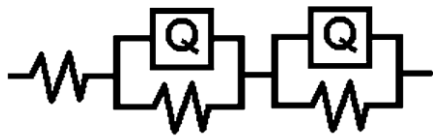


Figure 3. Experimental and fitted impedance of AA5083-H111 alloy samples without and with 24, 36 and 48 h shallow cryogenic treatment exposed to 3.5% NaCl



**Figure 4.** Equivalent circuit used for EIS analysis

The circuit R(QR)(QR) was recently used in our previous study [11]. The meaning of the elements in this circuit is as follows, respectively, for the solution resistance ( $R_s$ ), charge transfer resistance ( $R_{ct}$ ) and film resistance ( $R_f$ ) to be derived. The Q parameter denotes the constant phase element (CPE) and was used to compensate for the roughness and the non-uniformity of the studied metal electrodes;  $Q_f$  and  $Q_{dl}$  represent the capacitance for the surface film and double layer. All the derived electrochemical parameters are listed in Table 2.

It is clear from Fig. 3a and Table 2 that there was no significant change in the  $R_{ct}$  values with the cryogenic treatment or the duration of the process.

The increase in the  $R_f$  value indicated that the cryogenic process had created an oxide film on the metal surface. However, this increase was not directly proportional to the duration of the cryogenic treatment process.

The  $R_p$  ( $R_{ct}+R_f$ ) value was found to have increased from 33448 to 33984  $\Omega.cm^2$  after 48 h of cryogenic treatment.

These small changes seemed not to depend much on the duration time of the cryogenic treatment. In general, the  $R_p$  values were increased due to the small increases in  $R_{ct}$  and  $R_f$ .

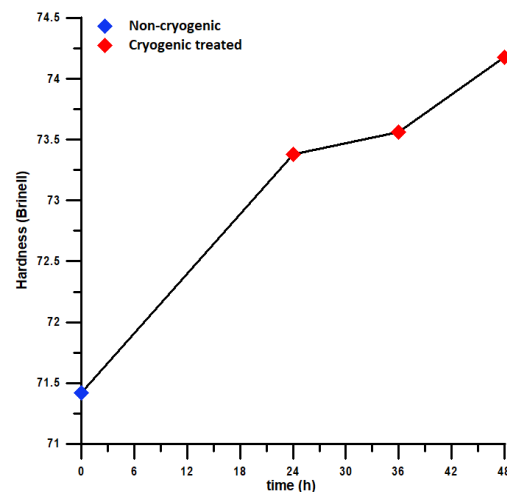
### 3.2 Hardness Testing

The hardness of all AA5083-H111 alloy samples was tested before the EIS experiments and a correlation was reported between the hardness and corrosion

**Table 2.** EIS results of AA5083-H111 in the 3.5% NaCl environment.

Investigated system	$R_s$ ( $\Omega.cm^2$ )	$Y_{01}$ ( $\Omega^{-1}s^2cm^{-2}$ ) $\times 10^{-3}$	$n_1$	$R_{ct}$ ( $\Omega.cm^2$ )	$Y_{02}$ ( $\Omega^{-1}s^2cm^{-2}$ ) $\times 10^{-3}$	$n_2$	$R_f$ ( $\Omega.cm^2$ )	$R_p$ ( $\Omega.cm^2$ )
Without cry treat.	18.60	0.153	0.7810	24954	0.118	0.9127	8494	33448
After 24 h cry treat.	18.86	0.162	0.7925	25310	0.018	0.9338	9248	34558
After 36 h cry treat.	18.28	0.027	0.8796	25650	0.213	0.9659	9424	35074
After 48 h cry treat.	19.62	0.0096	0.7936	24771	0.027	0.9879	9213	33984

resistance [12,13]. The hardness results are presented in Fig. 5. The hardness results indicated that there was very little difference in the data obtained depending on the time. The difference was 2.8 Brinell between the average hardness values of the metal samples cryogenically treated for 48 h and those not treated. This value shows that the cryogenic treatment process did not have a significant effect on the hardness of the AA5083-H111 alloy.



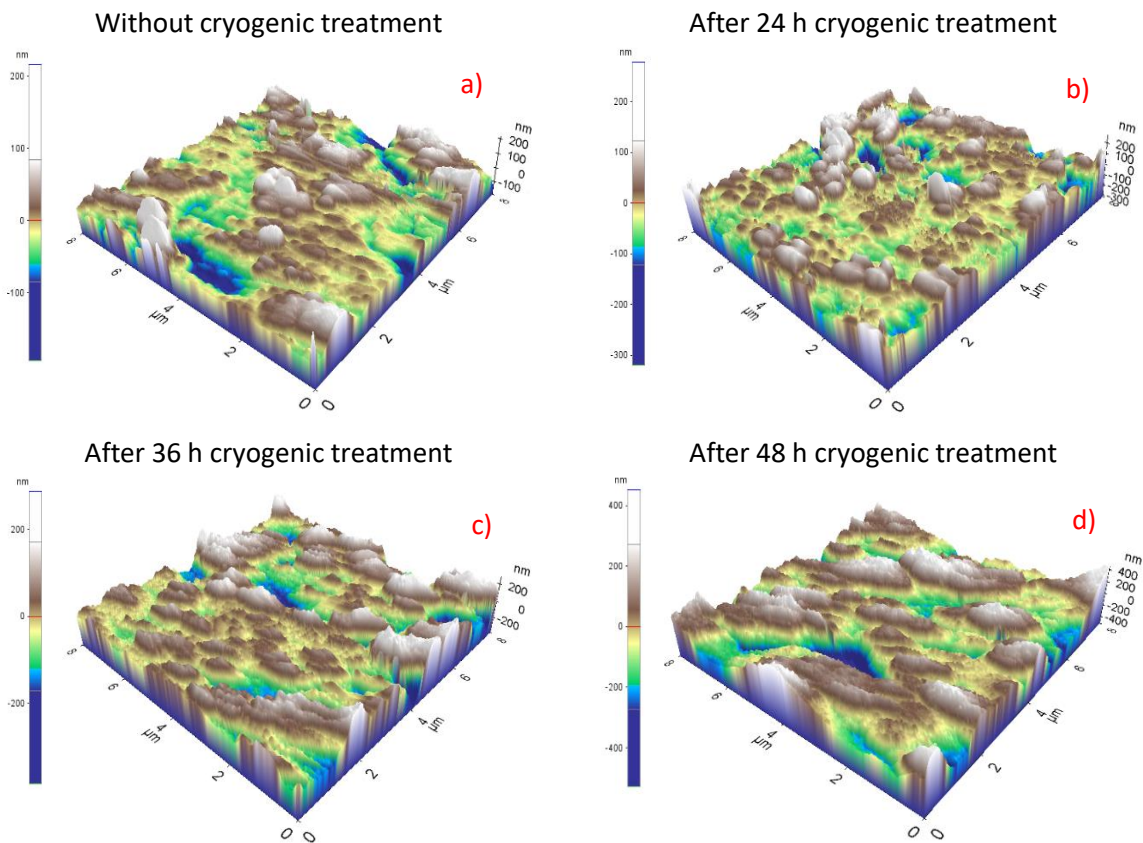
**Figure 5.** Surface hardness of AA5083-H111 alloy before and after 24-, 36- and 48-h cryogenic treatment

### 3.3 Surface Morphological Screening

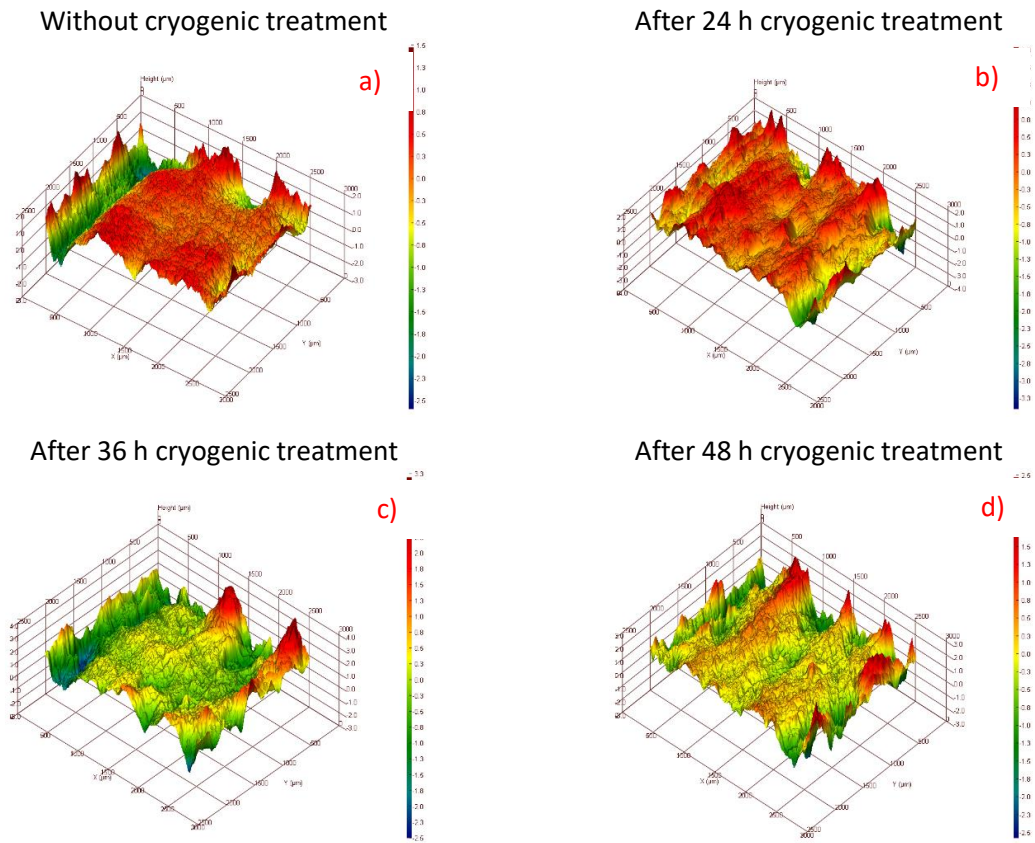
The surfaces of the AA5083-H111 samples with (24, 36 and 48 h) or without cryogenic treatment were examined with AFM following the EIS measurements.

**Table 3.** AFM results (horizontal axis)

	5083-H111	
	$R_a$ (nm)	$R_z$ (nm)
Without cry treat	47.874	213.921
After 24 h cry treat	75.650	315.969
After 36 h cry treat	126.872	403.466
After 48 h cry treat	183.892	731.526



**Figure 6.** AFM analyses of AA5083-H111 after EIS measurements.



**Figure 7.** OP analyses of AA5083-H111 after EIS measurements.



The average roughness of the AA5083-H111 sample surfaces was obtained by statistical analysis of the AFM images. For AFM image processing, the zero point of height corresponded to the plane surface (defined by the software), and the Z-scale showed both higher and lower features on the surface. The average roughness ( $R_a$ ) and root-mean-square roughness ( $R_z$ ) were calculated by the equations reported in [14].

The AFM images for the cryogenically treated and untreated samples are shown in Figs. 6a-6d. The average roughness of the non-treated surfaces was about 48 nm and as the time of the cryogenic process was increased from 24 h to 36 h and 48 h, this value increased respectively from 76 to 127 and 183 nm. The results are presented in Table 3. According to these EIS data, the cryogenic process formed an oxide film on the metal surface and protected the metal against corrosion. However, this oxide layer was not stable. Therefore, the roughness on the metal surface increased after the EIS measurements.

**Table 4.** OP results after EIS measurements.

	AA5083-H111	
	$R_a$ ( $\mu\text{m}$ )	$R_z$ ( $\mu\text{m}$ )
Without cry treat	0.07935	0.5173
After 24 h cry treat	0.1325	0.6587
After 36 h cry treat	0.1437	0.8998
After 48 h cry treat	0.1557	0.8496

The OP results were similar to the AFM findings (Figs. 7a-7d). The root-mean-square roughness ( $R_z$ ) value also increased with the cryogenic treatment duration time (Table 4).

#### 4. CONCLUSION

Investigations were carried out on the corrosion of AA5083-H111 in 3.5% NaCl solution and resulted in the following conclusions:

- The AA5083-H111 was highly resistant to corrosion in a 3.5% NaCl environment.
- Shallow cryogenic treatment ( $-80\text{ }^\circ\text{C}$ ) had no significant improvement effect on the corrosion of AA5083-H111 in 3.5% NaCl solution.

- There was a meaningful correlation between the EIS values and the hardness results. The findings obtained by both methods showed little change as the duration of the cryogenic process was increased.
- Results of the EIS measurements revealed that the charge transfer resistance increased with the duration of cryogenic treatment. However, this change was not extreme.
- The AFM and OP images revealed that the cryogenic treatment had changed the surface morphology of AA5083-H111. As the cryogenic treatment process time was increased, more roughness was observed on the metal surface after EIS measurements. In order to better explain this event, long-term studies should be conducted using Dynamic Electrochemical Impedance Spectroscopy (DEIS) in order to carry out time-based impedance analysis.
- The effect of deep cryogenic treatment on the improvement of corrosion of AA5083-H111 in 3.5% NaCl solution should also be investigated.
- According to these EIS data, the cryogenic process had caused an oxide film to form on the metal surface which protected the metal against corrosion. However, this oxide layer was not stable. This finding should be investigated using XRD and other methods.

#### ACKNOWLEDGEMENTS

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