Nanoscale Material Characterization Under the Influence of Aggressive Agents by Magnetic Force Microscopy and Opto-Magnetic Spectroscopy

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Keywords: metals, acids, characterization, Magnetic Force Microscopy (MFM), Opto-Magnetic Spectroscopy (OMS)

Abstract. Magnetic Force Microscopy (MFM) and Opto-Magnetic Spectroscopy (OMS) were used to characterize HTCV stainless steel and aluminum. Both materials were immersed in 1.0M HCl and 1.0M CH3COOH solutions for two hours. From the OMS method it was discovered that treated materials showed differences in peak wavelengths. Topographical and magnetic features for steel plate samples showed better resistance to an aggressive medium compared to aluminum. The results and analysis of these investigations are compared and presented in this paper.

Introduction

The corrosion of HTCV stainless steel and aluminum has received a considerable amount of attention. Despite their relatively limited resistance to corrosion, HTCV stainless steel and aluminum are widely used in large amounts in marine applications, nuclear and fossil fuel power plants, transportation, chemical processing, petroleum production and refining, pipelines, mining, construction, and metal-processing equipment. In solving a particular corrosion problem, a dramatic change in attack rate can often be obtained by altering the corrosive environment. Corrosion is a thermodynamically feasible process, because it is associated with a negative change in Gibbs free energy. It is the degradation of a metallic structure at its surface through the chemical reaction of the metal with a species in the environment. The serious consequences of corrosion have become a problem of worldwide significance. Practically every environment is corrosive to some extent, such as air and moisture; fresh, salt and mine waters; rural, urban and industrial atmospheres; steam and other gases like chlorine, ammonia, hydrogen and fuel vapour; and mineral acids like hydrochloric, sulfuric and nitric acid. Corrosion damage is not just limited to the appearance of the product, it can sometimes lead to catastrophic damage if ignored [1, 2, 3, 4].

The corrosion process is dependent on many parameters, such as environment, temperature, and metallurgical and chemical properties of metals [5]. In this paper, HTCV stainless steel and aluminum were studied as they are widely used in aerospace, naval, civil and nuclear engineering, due to their low cost, low density, and their high resistance to corrosion. These materials were subjected to pitting and film forming corrosion, as they are usually subjected to particles which play an important role in corrosion pit and film formation.

The films produced due to corrosion are weak and can breakdown further to form pits. The formation of pits due to corrosion is known to be one of the major damaging mechanisms affecting the integrity of these materials, and can cause failure in some cases [6, 7, 8, 9, 10]. To better understand the behavior of HTCV stainless steel and aluminum, and the corrosion that occurs on the surface of these materials, Magnetic Force Microscopy (MFM) and Opto-Magnetic Spectroscopy have been used. Results for both materials were compared to predict the forms of corrosion that can occur on their surface under specific corrosive environments.
Petrochemical plants have suffered continuous economic loss and human casualties due to metallic corrosion in H₂S-containing environments [1]. The salts and sulfide compounds dissolved in crude oil can provoke the formation of a corrosive aqueous solution whose chemical composition involves the presence of hydrochloric acid (HCl), acetic acid (CH₃COOH), and hydrogen sulfide (H₂S) [2, 3]. This corrosive aqueous solution is very aggressive and causes a variety of damage on HTCV stainless steel and aluminum during the operation of primary distillation plants. Acid solutions are generally used for pickling, industrial acid cleaning, acid descaling, oil well acidizing etc. [9]. Iron and its alloys, widely used in many industrial processes, can corrode during these acidic applications, particularly where hydrochloric acid and sulphuric acid are used.

Scanning probe microscopy (SPM) techniques are currently widely used in material surface characterization. The Atomic Force Microscope (AFM) was developed by Binnig, Quate, and Gerber in 1986 [11] and is a continuation of earlier technology – the Scanning Tunneling Microscope (STM) [12, 13]. Both technologies are based on point-to-point examination of the specimen by a sharpened tip probe. The AFM probe is a micro cantilever with a sharpened conical or pyramidal tip, whose length ranges from below 100 nm to over 250 nm. In this paper, measurements performed with MFM techniques are presented [14], with the intention of using them to examine the possibilities for process parameter optimization. Kojic et al. [14] used MFM in order to examine the relationship between structural and magnetic properties for different processing parameters. Process parameters were correlated with structural and magnetic properties, in the search for optimized process parameters. The resolution of the MFM was approximately 50 nm [15] which is better than standard magneto-optical techniques, although their combined use has been suggested for the purpose of verifying the interpretation of contrast in MFM.

White light was created using light emission diodes, and polarized white light using the same diodes under angles and distances selected to produce reflected polarized light. Digital images were created using a standard digital camera, also incorporating a lighting system and optical accessory. The view field had a diameter of 25 mm. The images in white and polarized light taken by the standard digital imaging tools were transformed into RGB color channel histograms. Using a specially developed algorithm, these histograms were converted into spectral distributions. These distributions, used in the blue and red channels as white minus polarized, were simple and gave characteristics such as the amplitude and position of the minima and maxima, which could be used for numerical characterization of the exposed matter. Of special interest were the following three composed convolutions of red minus blue, in white, polarized and white minus polarized. Very interesting characterizations of photographed substances appeared which were named the “opto-magnetic fingerprint” of matter [16]. As such, the purpose of the study was to examine the effects of HCl, a strong inorganic acid, and CH₃COOH, a weak organic acid, on the behavior of the HTCV stainless steel and aluminum under aggressive conditions at room temperature (25 °C) through Magnetic Force Microscopy (MFM) and Opto-Magnetic Spectroscopy (OMS).

Experimental Methods

In previous years, some very interesting results have emerged from the use of AFM/MFM techniques on various steel samples [15]. In the current study, HTCV stainless steel and aluminum were investigated using MFM and OMS as no known examinations had previously been performed with these materials.

Specimens were first cut into samples of dimensions 1.0×1.0×0.1 cm. These samples were inspected visually and then microscopically, for any imperfections on the surface. If sample had any imperfections then it was not used in the study. Surface imperfections can act as an initiation source of corrosion due to low corrosion resistance. After samples with no surface imperfections were selected, they were ground and polished according to the material.

The aluminum samples were ground on a grinding machine that used emery papers as the rotor. To ensure the grinding was done in a smooth manner, the samples were ground with different grits of emery paper, from rough to smooth. Aluminum samples were ground with 200, 500, 800 and 1200 grit emery paper. Initially, the sample was ground with 200-grid emery paper at 60 rpm for...
approximately 2 minutes. Water was used as coolant to remove all waste material. This process was then repeated for the 500 and 800 grit paper. When the sample was ground with 1200 grit emery paper, the speed was increased to 120 rpm for 4 minutes, to ensure that no sharp edges were left on the surface. The samples were then washed with fresh water and dipped into an ethanol solution to ensure complete removal of any waste from the surface. The samples were then polished using polishing plates with a 3 µm and 1 µm diamond spray. After polishing, the samples were washed with fresh water and taken for further cleaning.

After the samples were polished, they were cleaned using an ultrasonic cleaning machine. The samples were initially dipped into a diluted acetone solution, followed by a 70% ethanol solution, and finally distilled water (15 minutes per solution). After completing the cleaning process, the samples were removed from the ultrasonic cleaning machine and were allowed to dry under air. Once the samples were completely dry, an area of 2 µm x 2 µm was selected for the characterization study and the rest was coated with paint. The coating ensured that no corrosion was able to be formed on the surface of the samples except for the selected region.

The preparation method for the HTCV stainless steel samples was the same as for the aluminum, except that different grit emery papers (200, 400, 800 and 1200) were used in the grinding process. Both materials were immersed in 1M solution of HCl and in 1M solution of CH₃COOH for 2 hours. They were then dried in a flow of inert gas (argon), and experimental techniques described in Ronak [17] were applied.

**Opto-Magnetic Spectroscopy (OMS)**

The equipment used for imaging was a Canon digital camera, model IXUS 105, 12.1 MP. The light source was diffuse white light at Brewster’s angle (three LED’s set at an angle of 53˚ in relation to the vertical axes). The recording region was circular, with a diameter of approximately 25 mm.

When incident white light is diffused, the reflected white light is composed of electrical and magnetic components. However, diffused incident light inclined at a certain angle will produce reflected light which contains only an electrical component. This angle is called Brewster’s angle and it represents the magnitude of the angle of incidence at which the sample polarizes the incident light [18].

Both materials have a unique angle of light polarization. Since reflected polarized light contains an electrical component of light-matter interaction, taking the difference between white light (electromagnetic), and reflected polarized light (electrical), yields magnetic properties of matter based on light-matter interaction. As such measurements can identify the conformational state and change in tissue on a molecular level, this method was named the opto-magnetic fingerprint of matter or Opto-Magnetic Spectroscopy (OMS) [18].

In addition to a customized camera, custom designed software was used to analyse the images obtained, yielding a characteristic diagram (diagnostic result) showing the intensities of light corresponding to differences in wavelength. Since this light is polarized by the sample, it means that the character of polarization describes the character of the material. Therefore, by characterizing the reflected light, the characteristic properties of the sample can be identified.

This method is highly sensitive as it detects magnetic properties on the basis of the response to visible light excitation which is relatively low in energy [18].
Fig. 1. Experimental setup

Fig. 2. The opto-magnetic spectroscopy device consisting of a digital camera set on a Keyence magnifying system

Magnetic Force Microscopy (MFM)

Atomic Force Microscopy (AFM) is one of the methods that belong to a larger group called Scanning Probe Microscopy (SPM). This type of microscopy method uses a small probe with a sharp tip to scan across the sample in order to obtain surface information. The AFM technique is nowadays widely used in material surface characterization, and provides information about the structure on the nano-scale, the form of recorded structures (cavities), their distribution on the surface, and the total roughness of the scanned area. Magnetic Force Microscopy (MFM) is one of the varieties of Atomic Force Microscopy. However unlike AFM, MFM uses a probe tip coated with a thin film of ferromagnetic material.

This kind of probe tip will react to the magnetic domains on the sample surface. The image of the sample is obtained with a two-pass technique in which the initial scan is used to obtain the topography of the sample. In the second scan, the tip-sample distance is increased and the biased tip is scanned along the topography line obtained from the first scan.

The topographical line maintains constant tip sample distance, which equals the line of constant Van der Waals force. When the tip follows the topography line in the second scan the Van der Waals forces acting on the tip are kept constant. Thus, the only change in force affecting the signal is the change in the magnetic force.
Magnetic property evaluation is based on the magnetic force gradient image that shows the qualitative distribution of the magnetic field within the scanned area, pointing to the local distribution of carriers of magnetic properties [14].

In the present study, the SPM (Scanning Probe Microscope) system JSPM-5200 (JEOL, Japan) (Fig. 3) and magnetic material coated cantilevers from Nanosensors™, type PPP-MFMR were used (Fig. 4).

The Nanosensors™ PPP-MFMR AFM probe is a standard probe for MFM, providing a reasonable sensitivity, resolution and coercivity (Table 1).

The force constant of this probe type is specially tailored for magnetic force microscopy, yielding high force sensitivity while simultaneously enabling tapping mode and lift mode operation. The hard magnetic coating on the tip is optimized for high magnetic contrast and high lateral resolution of greater than 50 nm (guaranteed tip radius of curvature < 50 nm).

<table>
<thead>
<tr>
<th>Technical data</th>
<th>Nominal value</th>
<th>Specified range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness [µm]</td>
<td>3</td>
<td>2.0 – 4.0</td>
</tr>
<tr>
<td>Width [µm]</td>
<td>28</td>
<td>20 – 35</td>
</tr>
<tr>
<td>Length [µm]</td>
<td>225</td>
<td>215 – 235</td>
</tr>
<tr>
<td>Force Constant [N/m]</td>
<td>2.8</td>
<td>0.5 – 9.5</td>
</tr>
<tr>
<td>Resonance Frequency [kHz]</td>
<td>75</td>
<td>45 – 115</td>
</tr>
</tbody>
</table>

Fig. 3. Scanning probe microscope, JSPM-5200 from JEOL, Japan (NanoLab, Belgrade)

The Nanosensors™ PPP-MFMR AFM probe is a standard probe for MFM, providing a reasonable sensitivity, resolution and coercivity (Table 1).

The force constant of this probe type is specially tailored for magnetic force microscopy, yielding high force sensitivity while simultaneously enabling tapping mode and lift mode operation. The hard magnetic coating on the tip is optimized for high magnetic contrast and high lateral resolution of greater than 50 nm (guaranteed tip radius of curvature < 50 nm).

Fig. 4. SEM image of the Nanosensors PPP-MFMR probe tip
All images were generated using the tapping mode of the Atomic Force Microscope at a resolution of 256 x 256 pixels, on a scan area of 2 x 2 µm. All measurements were performed at room temperature and in a protected space. After scanning, all data was transferred to the WinSPM software package which allowed for further analysis of the images.

The WinSPM software package has the ability to execute multiple cross-sectional (profile) analyses of an image, and to obtain the roughness information of the whole image or a specific region. The maximum number of profile lines is five. This software can display a three-dimensional image (bird’s eye view) of the surface structure from the topography image of the AFM, which is very important for broader visualization of the topographic characteristic of the sample. The software displays results of the analysis of each profile.

The height $z$ at position $d$ along the line is defined as:

$$z = f(s)$$  \hspace{1cm} (1)

The height $Z_0$ of the centerline is defined as:

$$Z_0 = \frac{1}{L} \int_{0}^{L} f(s) ds.$$  \hspace{1cm} (2)

Roughness parameters that can be displayed are:

- Average of roughness ($R_a$):

$$R_a = \frac{1}{L} \int_{0}^{L} |f(s) - Z_0| ds.$$  \hspace{1cm} (3)

- Root mean square roughness ($R_q$):

$$R_q = \sqrt{\frac{1}{L} \int_{0}^{L} (f(s) - Z_0)^2 ds}.$$  \hspace{1cm} (4)

This is defined by a root mean square of the deviation of $f(s)$ from the centreline [19].

- 10-point average roughness ($R_{zijs}$):

$$R_{zijs} = \frac{1}{10} \left[ z_{p1} + z_{p2} + z_{p3} + z_{p4} + z_{p5} + z_{v1} + z_{v2} + z_{v3} + z_{v4} + z_{v5} \right]$$  \hspace{1cm} (5)

The 10-point average roughness is defined as the “sum of the average of the absolute values of the deviation from the centerline between the largest deviation and the fifth deviation, and the average of the absolute values of the deviation between the smallest deviation and the fifth deviation [19].”

The maximum difference between high (maximum value $Z$) and low (minimum max value $Z_{min}$) ($R_z$) [19] is:

$$R_z = R_{max} - R_{min}.$$  \hspace{1cm} (6)
Results and Discussion

The results acquired using Opto-Magnetic Spectroscopy, are shown in Fig. 5 and Fig. 6. Fig. 5(1) shows pictures taken in diffused light (left) and in polarized light (right). The result is the intensity - difference wavelength diagram, where peak values can be seen (Fig. 5(2)).

Fig. 5. (1) Pictures taken in diffused and polarized light; (2) Intensity - difference wavelength diagram of: (a) Untreated aluminum; (b) Aluminum treated with 1M acetic acid for 2h; (c) Aluminum treated with 1M hydrochloric acid.

Table 2 shows the average differences in peak values of the same material under different conditions. It can be seen that the wavelengths are slightly different whereas the intensities (amplitudes) of the peaks are very different (the differences are up to 7 units).
Table 2. Average peak values of wavelength difference and amplitude for untreated and treated aluminum

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average value of wavelength difference</th>
<th>Average value of amplitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>+ peak: 115.9; 126.6; 132.6; 144.7</td>
<td>2.9; 5.3; -4.6; -4.1</td>
</tr>
<tr>
<td></td>
<td>- peak: 107.7; 117.9; 130.1; 157.6</td>
<td>1.3; 7.3; -7.5; -1.9</td>
</tr>
<tr>
<td>(b)</td>
<td>+ peak: 117.5; 131.1</td>
<td>1.9; 3.1</td>
</tr>
<tr>
<td></td>
<td>- peak: 109.0</td>
<td>-2.8</td>
</tr>
</tbody>
</table>

Fig. 6. (1) Pictures taken in diffused and polarized light; (2) Intensity - difference wavelength diagram of: (a) Untreated HTCV steel; (b) HTCV steel treated with 1M acetic acid for 2h; (c) HTCV steel treated with 1M hydrochloric acid

Table 3 shows the average differences in peak values for HTCV steel under an aggressive medium. It can be seen that the wavelengths are slightly different whereas the intensities (amplitudes) of the peaks are very different (the differences are up to 10 units). The greatest peak
values are in case of HTCV steel treated with 1M hydrochloric acid, which was expected. Since 
HCl is monoprotic, meaning it dissociates completely, the H₃O⁺ concentration is much higher than 
the H₃O⁺ concentration in the acetic acid solution.

Table 3. Average peak values of wavelength difference and amplitude for untreated and treated 
HTCV steel

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average value of wavelength difference</th>
<th>Average value of amplitude</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>+ peak 113.0; 143.1</td>
<td>1.5; 1.2</td>
</tr>
<tr>
<td></td>
<td>- peak 105.9; 128.4; 163.4</td>
<td>-1.6; -1.6; -0.4</td>
</tr>
<tr>
<td>(b)</td>
<td>+ peak 124.2</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>- peak 109.8; 139.2</td>
<td>-2.3; -0.87</td>
</tr>
<tr>
<td>(c)</td>
<td>+ peak 115.1; 129.1</td>
<td>5.6; 2.8</td>
</tr>
<tr>
<td></td>
<td>- peak 107.5</td>
<td>-10.9</td>
</tr>
</tbody>
</table>

It is possible to detect the different influences of inorganic and organic acids on metals using the 
Opto-Magnetic Spectroscopy method. The acquired results were consistent. The Opto-Magnetic 
Spectroscopy method is a qualitative, not quantitative method that is used to characterize the 
surface structure of materials. The depth of a region of interest depends on the transparency of the 
sample, and can range from a few nanometers to a few millimeters. According to the acquired 
diagrams, it can be concluded that there were differences in peak wavelengths for both the untreated 
and treated metals. There were also different influences under aggressive conditions. The results 
acquired by MFM are shown in Figs. 7 - 12.

Fig. 7. (a) (Left) Topography image of an untreated aluminum sample. Scan size is 2 x 2 µm with 
maximum surface height 85.4 nm. The diagram below shows the arbitrarily selected profile line of 
the sample; (b) (Right) MFM image of the same area shown in (a)
Fig. 8. (a) (Left) Topography image of untreated HTCV steel sample. Scan size is 2 x 2 µm with maximum surface height 46.6 nm. The diagram below shows the arbitrarily selected profile line of the sample; (b) (Right) MFM image of the same area shown in (a)

Fig. 9. (a) (Left) Topography image of aluminum treated with 1M acetic acid for 2h. Scan size is 2 x 2 µm with maximum surface height 537.8 nm. The diagram below shows the arbitrarily selected profile line of the sample; (b) (Right) MFM image of the same area shown in (a)
Fig. 10. (a) (Left) Topography image of HTCV steel treated with 1M acetic acid for 2h. Scan size is 2 x 2 µm with maximum surface height 566.6 nm. The diagram below shows the arbitrarily selected profile line of the sample; (b) (Right) MFM image of the same area shown in (a)

Fig. 11. (a) (Left) Topography image of aluminum treated with 1M hydrochloric acid for 2h. Scan size is 2 x 2 µm with maximum surface height 1470 nm. The diagram below shows the arbitrarily selected profile line of the sample; (b) (Right) MFM image of the same area shown in (a)
Fig. 12. (a) (Left) Topography image of HTCV steel treated with 1M hydrochloric acid for 2h. Scan size is 2 x 2 µm with maximum surface height 668.3 nm. The diagram below shows the arbitrarily selected profile line of the sample; (b) (Right) MFM image of the same area shown in (a)

Table 4. Obtained topography image parameters for both materials

<table>
<thead>
<tr>
<th></th>
<th>Aluminum prior to acid treatment</th>
<th>Aluminum after treatment with 1M acetic acid for 2h</th>
<th>Aluminum after treatment with 1M hydrochloric acid for 2h</th>
</tr>
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<tbody>
<tr>
<td>( R_z ) [nm]</td>
<td>85.4</td>
<td>537.8</td>
<td>1470.0</td>
</tr>
<tr>
<td>( R_a ) [nm]</td>
<td>12.7</td>
<td>71.1</td>
<td>180.0</td>
</tr>
<tr>
<td>( R_q ) [nm]</td>
<td>16.0</td>
<td>90.4</td>
<td>224.6</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>HTCV steel prior to acid treatment</th>
<th>HTCV steel after treatment with 1M acetic acid for 2h</th>
<th>HTCV steel after treatment with 1M hydrochloric acid for 2h</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_z ) [nm]</td>
<td>45.9</td>
<td>566.6</td>
<td>668.3</td>
</tr>
<tr>
<td>( R_a ) [nm]</td>
<td>5.33</td>
<td>63.1</td>
<td>93.1</td>
</tr>
<tr>
<td>( R_q ) [nm]</td>
<td>6.81</td>
<td>79.6</td>
<td>116.8</td>
</tr>
</tbody>
</table>
A comparison of the results highlighted the differences in topography images for all three samples of each material. As evident from the topographies, Figs. 7(a) – 12(a), it was possible to determine how much acid altered the surface of the material. One of the most important characteristics of the topography images that were compared is the maximal height $R_z$, which is shown by the scale at the right of the image. Another important feature is the average roughness, $R_a$, which is shown along the chosen profile line. For both materials, $R_a$ and $R_z$ were very different before and after the acid treatment (Table 4). For untreated aluminium, $R_a$ was initially 12.7 nm, however after acetic acid treatment, it changed to 71.7 nm (approximately 5 times more). The aluminium sample suffered even greater surface destruction after the hydrochloric acid treatment. A similar observation was made for the HTCV steel sample, however the acids were much less destructive to its surface than they were for the aluminium. For all materials, the gradient of magnetic field data showed negative values in phase shift angles. According to our previous MFM unpublished results of copper (as a diamagnetic example) and aluminium (which is paramagnetic), strictly negative magnetic field gradient phase shift angles correspond to paramagnetic materials. On the other hand, if phase shift angles change signs (have positive shifts), this indicates that the materials possess diamagnetic properties. As such, it can be concluded that both investigated materials have paramagnetic properties.

**Conclusion**

Magnetic Force Microscopy offers the possibility of measuring topography features on the micro, nano and pico scale. The same level of precision applies for undertaking measurements of physical quantities, such as magnetism and electrical properties. Opto-Magnetic Spectroscopy (OMS) is very sensitive since it detects magnetic properties on the basis of response to visible light excitation which is relatively low in energy.
Both of these methods were used for the characterization of HTCV stainless steel and aluminum which had been treated with 1.0M HCl and 1.0M CH₃COOH solutions.

Results showed nano-scale differences between untreated materials and materials treated with aggressive agents. Comparing MFM results with those obtained using OMS, it was found that structural changes of materials at the nano level are more pronounced under the influence of strong acids. Furthermore, acids are much more destructive to the surface of aluminium than they are to HTCV steel.

References


