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Aluminium alloy corrosion detection by magnetic measurements

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During corrosion, currents passing from anodes to cathodes generate magnetic fields. Pitting corrosion of aluminium alloys in aggressive media was detected through magnetic field measurements, without electrical connection to the sample and without reference or auxillary electrodes in the corrosion cell. A sodium chloride solution containing hydrogen peroxide or a solution of potassium hydroxide 2 mol l^{-1} solution was used for corrosion tests. Two magnetometers developed by LETI were used: a superconducting quantum interference device (SQUID) magnetometer and a nuclear magnetic resonance (NMR) magnetometer. The SQUID provided information on spatial distribution and direction of the currents. The NMR magnetometer was better for studying the development of the corrosion over time. *© 1998 Kluwer Academic Publishers*

1. Introduction

When corrosion occurs, the current circulates from a cathodic site to an anodic site in the metal with looping in the corrosion cell. The distribution of the corrosion currents on an electrode is very complex. It depends on many factors, such as the presence of metallurgical heterogeneities, the electrolyte, and the geometry of the electrode and the container.

In conventional corrosion studies, the measurement probes have to be placed in the electrolyte in order to determine the corrosion current. Consequently, the electrodes may disturb the current distribution. Furthermore, in some cases, it is difficult, if not impossible to insert the probe in the electrolyte.

The circulation of an electrical current creates a magentic field that depends on the amplitude and the distribution of this current. Conversely, the measurement of the magnetic field induced by corrosion current loops should provide information on the amplitude and the spatial distribution of the corrosion current.

The first studies undertaken on this subject were conducted at the Massachussetts Institute of Technology with a superconducting quantum interference device (SQUID) magnetometer [1, 2]. The authors showed that the magnetic fields induced by the reactions associated with zinc corrosion in an HCl solution were detectable despite their very weak intensities. U-shaped zinc electrodes coated with an epoxy resin were used and only the faces of the branches of the U were exposed to the electrolyte. In this configuration, the measured magnetic signal was comparable to the field induced by a current loop (magnetic dipole).

The same laboratory found that this measurement technique compared favourably with more conventional electrochemical methods of current measurement. Magnetic measurements have been used to study electrochemical noise [3], for cyclic voltametry [4], to differentiate uniform and dendritic electrodeposition [4], and to determine the susceptibility of resistant and sensitive steels to intergranular corrosion [5].

Murphy *et al.* [6] used the SQUID magnetometer to identify local corrosion sites on buried pipelines through the measurement of interfacial currents produced by weak applied voltages. Poulbot *et al.* [7] also used the SQUID magnetometer to study zinc idiomorphic corrosion. The results, and an associated two-dimensional model, were used to establish the geometrical distribution of the corrosion current. Moreover, by using the nuclear magnetic resonance (NMR) probe [8] developed at the LETI, they were able to measure temporal fluctuations in the magnetic-field induced corrosion of the U-shaped zinc electrodes.

More recently, Li *et al.* [9] measured non-invasively three different types of *in situ* active corrosion using

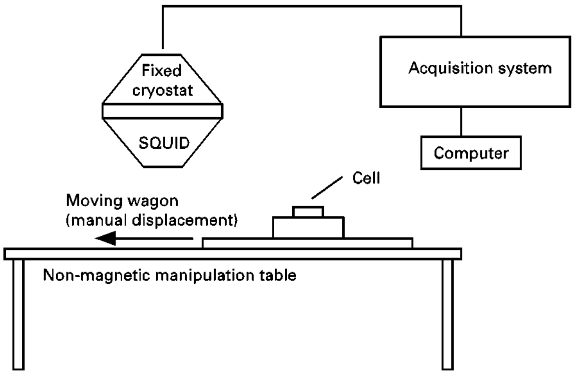

Figure 1 SQUID measuring equipment [7].

a SQUID magnetometer. They show that a higher corrosion rate results in a more intense magnetic field and that the SQUID magnetometer was sensitive to corrosion activity occurring on the opposite side of a plate specimen.

The aim of the present study was to evaluate aluminium alloy corrosion using magnetometric techniques. More specifically, the objective was to detect pitting corrosion in aluminium alloys with the help of a SQUID magnetometer and the NMR probe, the latter being used to monitor the phenomenon over time.

2. Experimental procedure

2.1. SQUID magnetometer

The SQUID magnetometer has a second-order gradiometer flux transformer, and detects only a magnetic component. The sensitivity rating is of the order of a few picoteslas [7].

Measurements were conducted in an amagnetic room, remote from the laboratory, in order to limit electromagnetic disturbance. A diagram of the measuring equipment is shown in Fig. 1.

The magnetic field variations induced by the passage of the electrochemical cell were measured by the SQUID through the movement of the wagon. The distance between the sample and the bottom of the cryostat was constant at 15 mm.

2.2. NMR magnetometer

The LETI develops high-resolution magnetometers based on the principle of nuclear magnetic resonance (NMR) amplified by the Overhauser effect [8]. The NMR probe continuously measures the modulus of the earth's magnetic field. Through the use of a reference probe and differential measurements, it is possible to eliminate the temporal variations of the earth's magnetic field and measure only the magnetic disturbance induced by the corrosion in the test probe. The system has a resolution of several picoteslas and has a good signal-to-noise ratio. These tests were carried out at the LMMCF, one of LETI's measuring sites, which is not affected by electromagnetic perturbations.

The temporal variations in the differential signal between the test probe and the reference probe were measured and an HP 3561 signal analyser was used to plot the power spectral density (PSD) versus frequency. Frequential analysis of the magnetic noise was used to detect periodic phenomena.

2.3. Aluminium alloys

The characteristics of the aluminium specimens used (Pechiney–CRV) are given in Table I.

2.4. Electrochemical cell and corrosive solution used with the SQUID magnetometer

The electrolyte used is that used in the ammonium salt solution exfoliation test (ASSET) corrosion test [10]. Its composition is as given in Table II. This solution induces marked pitting corrosion of the aluminium due to its strong concentration in chloride ions and the presence of hydrogen peroxide. Its oxidizing power decreases with time through the deterioration of the hydrogen peroxide. Solutions used must therefore always be freshly prepared.

The electrochemical cell was a Petri box filled with corrosive solution.

The aluminium plate ($50 \times 80\,\mathrm{mm}^2$) was placed on the bottom of the box and was always oriented in the same way under the SQUID bench.

2.5. Electrochemical cell and corrosive solution used with the NMR probe

First, a glass tube filled with ASSET solution was used as the electrochemical cell. A 35 mm × 110 mm plate of 3003 alloy was placed in the tube which was then corked. Next, a 1070 alloy pot (height 63 mm, diameter 25 mm) was used. This was filled with ASSET

TABLE I Characteristics of aluminium alloys used

Reference	1199	1200	1070	3003
State	H18	H18	H1X	H18
Thickness (μm)	360	280	250	310
Chemical composition	Fe 9 p.p.m.	Fe 0.61%	Fe $< 0.25\%$	Fe 0.6%
	Si 13 p.p.m.	Si 0.16%	Si $< 0.20\%$	Si 0.2%
	Mg 2 p.p.m.	Mg 10 p.p.m.	Mg $< 0.03\%$	Mg $< 0.02\%$
	Mn 10 p.p.m.	Mn 90 p.p.m.	Mn $< 0.03\%$	Mn $< 1.09\%$
	Ti 2 p.p.m.	Ti 0.015 p.p.m.	Ti $< 0.03\%$	Ti $< 0.05\%$
	Cu 41 p.p.m.	Cu 0.01 p.p.m.	Cu $< 0.03\%$	Cu $< 0.05\%$
	Cr 2 p.p.m.	–	Zn $< 0.7\%$	Cr 0.01%
	Ga 3 p.p.m.			Zn 0.01%

TABLE II Composition of the ammonium salt solution exfoliation test (ASSET solution)

Ammonium chloride (NH_4Cl)	1 mol l^{-1}
Ammonium nitrate (NH_4NO_3)	0.25 mol l^{-1}
Ammonium tartrate ($(NH_4)_2C_4H_4O_6$)	0.01 mol l^{-1}
Oxygenated water (H_2O_2)	0.3 (% vol)
pH: 5.2–5.4	

TABLE III Equivalent corrosion current densities of aluminium ($\mu A\,cm^{-2}$)

	Aluminium alloy		
	1199	1200	3003
$i_{corr}(t = 24\,h)$	10	91	89
$i_{corr}(t = 48\,h)$	24	16	441
$i_{corr}(t = 72\,h)$	14	67	228

solution and corked. In both cases, the cell was placed horizontally in the NMR probe.

2.6. Evaluation of the oxidizing power of the ASSET solution on aluminium alloys

The weight losses of the 1199, 1200 and 3003 aluminium alloys placed in the ASSET solution were measured after 24, 48 and 72 h immersion. The corresponding corrosion current densities are given in Table III.

The surface considered is the total surface of the sample. In the case of pitting corrosion, the real surface is difficult to evaluate and varies at any one time.

After 4 h in the ASSET solution, examination of the surface of the three alloys revealed that they had undergone pitting corrosion (Figs 2–4). Pit diameter and depth were the same for all the samples.

3. Results and discussion

3.1. Results of tests using the SQUID magnetometer

Experiments using the SQUID magnetometer showed that the cell and the alloys, either in air or in distilled water, induced no significant magnetic signal.

Tests were conducted first on the 3003 alloy in the ASSET solution. The induced magnetic field was measured peak-to-peak as a function of the immersion time in the corrosive solution. An example of the signal measured by the SQUID is given in Fig. 5.

These measurements show that the detected magnetic field was effectively due to corrosion because it was not measured for the alloy sample alone nor in distilled water, nor for the reference solution.

The shape of the signal measured by the SQUID magnetometer varied over time. Polarity changes were observed during the experiment. In addition, by turning the plate over, the direction of the measured induced dipole was reversed.

Two different phases of corrosion were observed in the first 4 h immersion:

Figure 2 Micrograph of the 1199 alloy after 4 h immersion in the ASSET solution, × 500.

Figure 3 Micrograph of the 1200 alloy after 4 h immersion in the ASSET solution, × 500.

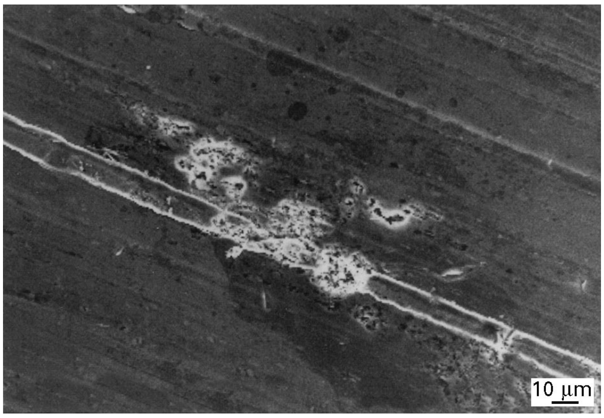

Figure 4 Micrograph of the 3003 alloy after 4 h immersion in the ASSET solution, × 500.

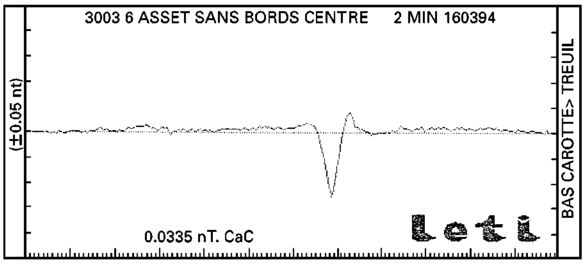

Figure 5 Signal measured by the SQUID magnetometer for the 3003 alloy after 2 min immersion in the ASSET solution.

(i) a decreasing signal during the first 2 h. This stage would be caused by hydrolysis of the passive layer and the start of pitting on defects in this layer;

(ii) stabilization of the signal. This stage would correspond to the growth of the pits which had already started to form.

Three tests were conducted for each alloy: the first on a bare plate, the second on a plate with varnished edges, and the third on a plate with the lower side and edges varnished. In addition, and attempt was made to map the induced dipoles on the plates through three passages under the SQUID magnetometer. Indeed, because in our operating conditions the resolution of the machine widthwise was 35 mm, three passages of the plate positioned lengthwise, parallel to the direction of passage under the SQUID magnetometer, would be sufficient to map the plate.

According to the results obtained, varnishing of the edges decreased the amplitude of the signal. This is due to the fact that pits begin preferentially on the edges. Varnishing one side also decreased the amplitude of the signal because, in this case, there was only one corroding side. It also eliminated polarity inversions probably due to movements of the electrolyte between the upper side and lower side of the plate. Signals corresponding to the centre, left and right parts of the plate have comparable amplitudes but different shapes, which also vary over time.

Variations in the magnetic field measured peak-to-peak with the SQUID magnetometer were plotted against immersion time in the ASSET corrosive solution for 3003, 1200 and 1199 alloys (Fig. 6). The lower side and edges were varnished.

It was not possible to use a comparison of signal amplitudes for the three alloys to identify the specific sensitivity to corrosion of each alloy. In fact, for samples with one side and the edges varnished, the 1200 alloy exhibited a magnetic signal greater than the 3003 alloy, while it is less sensitive to corrosion. To differentiate these alloys in a pitting solution and in a solution producing generalized corrosion, we measured the magnetic field induced by these alloys in a KOH 2 mol l^{-1} solution. One side and the edges of the plates were varnished. Changes in the magnetic field with time, as detected by the SQUID magnetometer, are as follows (Fig. 7). According to the curves obtained, the signal was clearly superior in the case of generalized corrosion in the KOH 2 mol l^{-1} solution. The 1200 and 3003 alloys seem to have comparable behaviour in the potash, and corroded more strongly than the 1199 alloy. This result was confirmed by the weight loss measured on aluminium alloys in KOH 2 mol l^{-1} solution (Table IV). The SQUID magnetometer can thus underline the sensitivity of different alloys to the various types of corrosion.

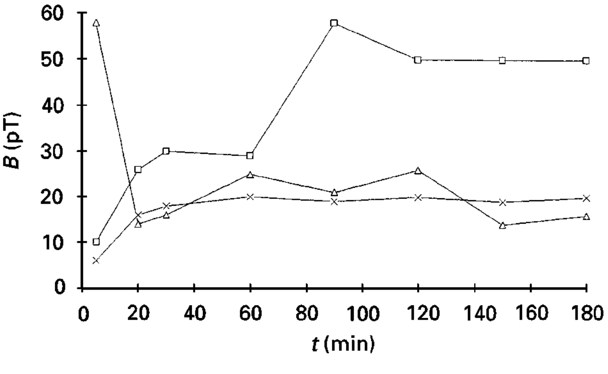

Figure 6 Change with time of the signal measured by the SQUID magnetometer for the ASSET solution: (×) 3003 alloy, (□) 1200 alloy, (△) 1199 alloy.

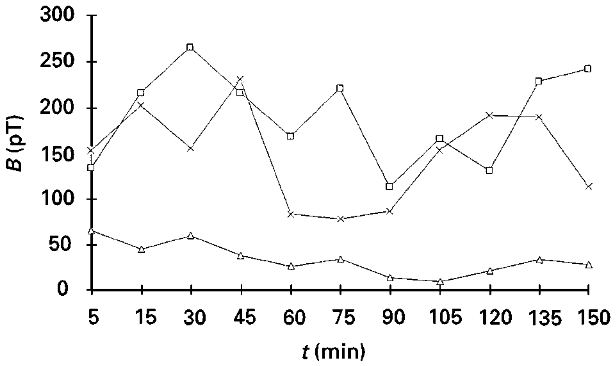

Figure 7 Changes over time in the signal measured by the SQUID magnetometer for the KOH 2 mol l^{-1} solution: (△) 1199 alloy, (□) 1200 alloy, (×) 3003 alloy.

TABLE IV Equivalent corrosion current densities of aluminium alloys in KOH 2 mol l^{-1} solution

	Aluminium alloy		
	1199	1200	3003
i_{corr}(mA cm^{-3})	7.4	17.4	31.5

3.2. Test results using the NMR magnetometer

3.2.1. Test undertaken on an aluminium alloy plate

For the 3003 alloy, which was degaussed beforehand, the differential signal was measured after 1 immersion in the ASSET corrosive solution. The PSD is shown in Fig. 8 with peaks at 3.2 and 6.4 mHz. These peaks were not observed in the absence of the sample and were not caused by interference between the two probes. A periodic electrochemical phenomenon was thus detected which may have been the initiation and repassivation of pits.

3.2.2. Test undertaken on an aluminium alloy pot

The power spectral density of the differential NMR signal was recorded first for the empty, corked pot and then for the pot filled with the ASSET solution and corked, at different times, and finally for the empty, corked pot.

After 1h testing for the pot filled with the ASSET solution, a new peak on the PSD was observed at 22.5 mHz. Corrosion was thus detected inside a cylin-

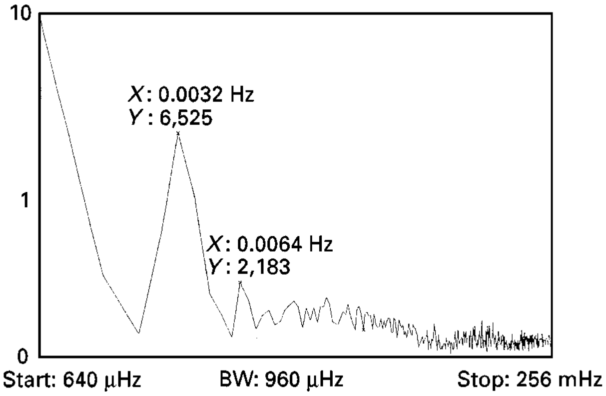

Figure 8 Power spectral density for the 3003 alloy in the ASSET solution.

drically shaped sample. Non-invasive corrosion in an entirely closed container can only be detected otherwise by measuring induced magnetic fields, which underlines the interest of this particular technique.

4. Conclusion

It has been shown that pitting corrosion can be detected in aluminium alloys using a SQUID magnetometer. Changes in the shape of the signal over time vary with each alloy.

The signal tends to stabilize with time when the maximum density of the pits for the alloy in the studied environment is reached. Moreover, the SQUID magnetometer can be used to show the differing sensitivities of aluminium alloys to generalized or pitting corrosion. The NMR probe was used to measure a characteristic frequency of the signal for the 3003 alloy in the ASSET solution. Corrosion was also detected inside samples in the form of a pot. However, lack of knowledge of current loops on the surface prevented us from linking the magnetic field measurements to the corrosion current. Magnetometers provide qualitative information on corrosion intensity but without calibration they give no quantitative information.

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