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Investigation of quasi-stationary magnetic fields of corrosion currents of zinc-copper cells using giant magneto-impedance magnetometer

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ABSTRACT

A scanning giant magneto-impedance (GMI) magnetometer has been used to measure small magnetic fields of corrosion currents in zinc-copper cells. In situ magnetic images of the copper plates with one or two small anode (zinc) inclusions of different sizes located at various distances at the sample surface have been obtained. To interpret the magnetic images of the corrosion currents a numerical simulation program has been developed. A good qualitative agreement between experimental and theoretical results proves that the scanning GMI magnetometry is a promising tool for in situ investigation of some of local corrosion processes.

1. Introduction

Many types of corrosion destruction of metallic materials and coatings in aqueous solutions are related with the local micro galvanic elements acting at corroding surface [1]. The ion and electron currents flowing between the local anode and cathode give rise to the corresponding local magnetic fields. The development of the magnetic methods of corrosion control seems promising for in situ studies of corrosion of various metals and coatings and for corrosion monitoring of equipment during operation. Therefore, in the papers [2–6] there were attempts to register the magnetic fields of corrosion currents using sensitive magnetometers.

The Superconducting Quantum Interference Devices (SQUIDs) were the first magnetometers that have been used in efforts [2–5] to measure magnetic field of corrosion currents. These magnetometers have outstanding sensitivity to magnetic field, better than 10^{-10} Oe. Unfortunately, the SQUID sensor was not located immediately in the solution [2–4], close enough to the corroding surface. In the majority of the studies [2–5] only the magnetic field component normal to the corroding surface was measured. In our opinion this is one of the limitations of the SQUID measurement, since in many cases the tangential component of the magnetic field of corrosion current considerably exceeds the normal one. We would like to note also, that the results of SQUID measurements are not always convincing. For example, the distribution of the magnetic field measured is not directly correspond [2] to the surface microstructure after corrosion. Thus, it seems reasonable to conclude that up to now the SQUID magnetometers were unable to register the actual distribution of the magnetic fields of corrosion currents of local micro galvanic elements working at the corroding surface.

The magnetometer based on giant magnetoresistance (GMR) sensor [6] was used for the first time as non-cryogenic type magnetometer to measure magnetic fields set up by corrosion currents. The measured magnetic fields were shown to correlate to corrosion rate through direct measurement. However, the tests were done without any sort of shielding from external magnetic field. The authors of Ref. [6] pointed out that they were unable to measure explicitly the local magnetic field distribution called them “magnetic field of an individual electrochemical phenomenon”, but conclude that a uniformly corroding surface is magnetically emissive.

Recently [7], a very small tangential component of magnetic field of corrosion current, of the order of 10^{-4} Oe, has been directly measured for the first time using the giant magneto-impedance (GMI) magnetometer [8,9] with a sensitivity of about 10^{-6} Oe. In contrast to the SQUID magnetometer, it does not require cryogenic

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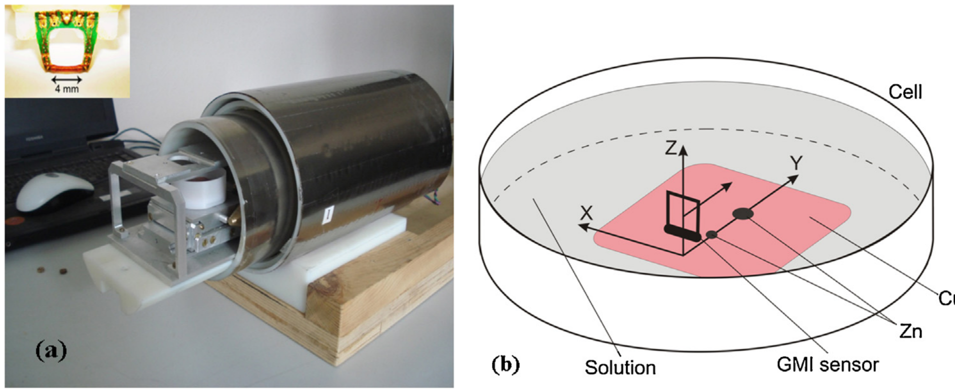

Fig. 1. (a) General view of the GMI scanner within a two-fold magnetic shield. The residual magnetic field within the shield, $H_r \approx 0.4–0.5$ mOe, is 1000 times smaller than the Earth's magnetic field, $H_E \approx 500$ mOe. Inset in (a) shows the general view of the GMI sensor. (b) Position and direction of movement of the GMI sensor within the solution.

cooling. Besides, the GMI sensor can be positioned in close proximity (less than 0.5 mm) to the corroding surface of any configuration. This provides a reasonable spatial resolution required for a reliable detection of weak magnetic field of corrosion currents. In Ref. [7] the possibility of direct measurement of the magnetic field of corrosion currents has been demonstrated for a model zinc-copper cell placed in a weak solution of sulfuric acid. The sample studied was a copper cylinder with a small cylindrical zinc inclusion in its center. In addition to the experimental demonstration, for cylindrically symmetric inclusion an explicit theoretical expression has been obtained for the distribution of the magnetic field and corrosion currents in the electrolyte using Waber's boundary condition [1,10] for the electrical potential at the metal—electrolyte interface. The total corrosion current of the inclusion has been estimated directly from the magnetic field distribution measured. For comparison, the loss of the sample mass was directly measured by conventional gravimetric method.

In the present paper the scanning GMI magnetometer is used for the experimental study of the magnetic field distribution created by corrosion currents in more complicated zinc-copper samples with one or two anode (zinc) inclusions of different sizes located at various distances. In addition, a numerical simulation program is developed capable to calculate the distribution of magnetic fields of corrosion currents for a sample containing randomly distributed anode (cathode) inclusions of different diameters at the sample surface. The theoretical calculations are in a good qualitative agreement with the results of magnetic measurements. This confirms the possibility of using scanning GMI magnetometry for in situ studies of some of local corrosion processes.

2. Material and methods

The sensing element of the GMI magnetometer is a piece of glass-coated amorphous ferromagnetic microwire of 0.5 cm in length, the diameter of the mirowire magnetic nucleus being about 20 μm. The GMI voltage is generated in a tiny coil of length 4 mm and diameter 0.5 mm that is wound around the microwire [8]. The GMI sensor is mounted on the lower ends of the U-shaped holder. The lead wires from the electronic circuit of the GMI magnetometer are attached to the upper part of the holder. The lower part of the GMI sensor was sealed with several layers of polymeric adhesive to allow its use in aggressive solutions. The U-shaped holder of the GMI sensor was designed to ensure unimpeded movement of the fluid around the sensor. The overall view of the GMI sensor is shown in the inset in Fig. 1a.

The calibration of the GMI sensor was performed in a uniform magnetic field of the Helmholtz coils. The transfer coefficient of the GMI sensor was measured to be 2.75 mOe per 1 V of the output voltage. The measuring interval of the GMI magnetometer is given by ±13 mOe. To eliminate the influence of the Earth magnetic field (about 500 mOe) all measurements were performed inside a two-fold permalloy shield. It provides the shielding of the permanent and low frequency magnetic fields more than 1000 times. A general view of the measuring system with the magnetic shield is shown in Fig. 1a.

To measure the local magnetic field of corrosion currents the nonmagnetic *X-Y* scanner was used, where the GMI sensor was positioned horizontally parallel to the *x*-axis at a fixed elevation $z = 0.4–2$ mm above the sample surface. During the measurement the mobile platform with the sample is moved by a stepper motor with respect to the GMI sensor along the *y*-coordinate.

Specimen geometry and location of the GMI sensor during scanning are shown in Fig. 1b. The sample is continuously moved relative to the GMI sensor at a constant velocity 1 mm/sec. A typical scan length was 20–25 mm. Signal recording was performed at a rate of 10 points per second. The *x*-component of the magnetic field created by the corrosion currents, $H_X(y)$, was recorded as a function of the *y* coordinate along the sample surface. The bandwidth of the measurement system was 30 Hz. Due to high enough signal to noise ratio no additional signal processing before recording was carried out. Specialized GMI sensor for weak magnetic field measurement, non-magnetic scanner and magnetic shield were manufactured by Ltd. «MaCryElsystems» [9].

Three zinc-copper samples were prepared for in-situ corrosion studies using GMI magnetometer. The samples consisting of thick (∼1 cm) square copper plates with a side of 3.0 cm (copper content not less than 99.95%) had small cylindrical zinc inclusions (zinc content was at least 99.98%). The sample #1 had one zinc inclusion of 0.2 cm in diameter. The sample #2 contained two zinc inclusions of 0.2 cm in diameters shifted along the *y*- axis at a distance $dY = 0.3$ cm from each other. In the sample #3 two zinc inclusions of diameter 0.15 and 0.25 cm were arranged along the *y*-axis at a dis-

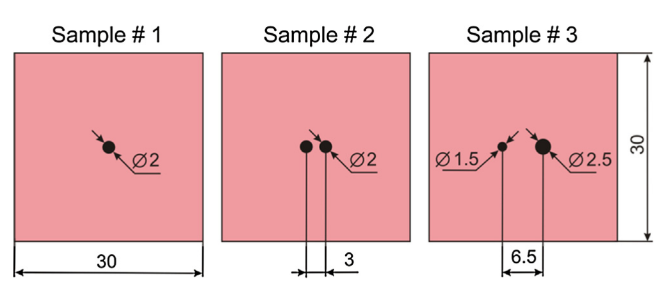

Fig. 2. Geometry of the experimental samples studied. The sizes are given in mm.