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Microelectrode techniques for corrosion research of iron

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ABSTRACT

Two micro-electrode techniques, scanning electrochemical microscopy (SECM) and the micro-capillary cell (MCC) technique, were used to investigate corrosion behaviour of a polycrystalline iron surface in acidic sulphate media. Local corrosion reactivity was found to be strongly dependent on crystallographic orientation of the surface as well as measurement conditions. Results obtained by using microelectrode techniques are expected to reveal all aspects of corrosion behaviour of the surfaces of polycrystalline materials including iron.

1. Introduction

Iron is the most commonly used metal in industry. Corrosion behaviour and passivity of iron are understood well [1]. However, most metallic materials, including iron, are generally polycrystalline. Thus, it is important to investigate corrosion behaviour of iron surfaces from the viewpoint of crystallography since crystallographic aspects have not been elucidated due to a lack of methods for investigating these aspects. A corroding specimen surface has conventionally been investigated by using electrode techniques. The use of a potentio/galvanostat with three electrodes, working, counter and reference electrodes, is a typical polarisation technique and provides information on electrochemical aspects of the surface such as corrosion potential and corrosion current. However, information obtained by this conventional technique corresponds to the whole surface immersed in an electrolyte solution. In order to investigate the surface in more detail, micro-electrochemical techniques are necessary.

Many micro-electrochemical techniques have been developed and have been used for investigation of a non-uniform reaction or localised reaction on a surface. Roughly, these techniques can be classified into techniques for scanning a microprobe over the surface and techniques for making the surface area smaller. In the former, various physicochemical phenomena can be used as the scanning probe to obtain local information on the surface. For example, in situ scanning tunnelling microscopy shows the

passive surface morphology of copper [2] and nickel [3] on an atomic scale. A synchrotron X-ray beam has been used to obtain diffraction patterns of a passive film on iron [4] and diffraction patterns of salt films on dissolving metal surfaces in artificial corrosion pits [5]. These probes are used in an electrochemical cell and enable non-electrochemical surface information to be obtained. On the other hand, an electrochemical probe is effective for obtaining electrochemical information directly from the surface. Amperometric and potentiometric microelectrode probes are used in scanning electrochemical microscopy (SECM) [6,7] and the scanning vibrating electrode technique (SVET) [8,9], respectively. In the latter, masking techniques are available for excluding the surface area other than the specimen area in a submillimetre scale. Schultze et al. used photo-resist coating to address the specimen part and to limit the surface area for anodisation of a titanium single grain surface [10]. The micro-capillary cell (MCC) technique is also effective for obtaining electrochemical information from a limited area of the surface and has been used to investigate a local material surface [11,12]. In this paper, applications of SECM and MCC technique for the investigation of a corroding iron surface are mainly reviewed.

2. Microelectrode technique

An electrode with a very small surface area compared with that of a general electrode is called a microelectrode. However, an electrode with a characteristic length of less than several tens of micrometres shows a unique electrochemical behaviour in a mass-transfer process. This unique behaviour is caused by diffusion of

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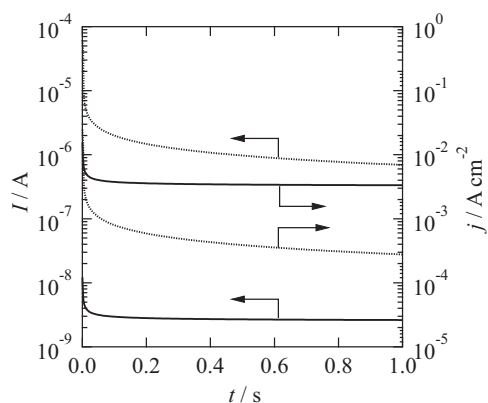   *E-mail address:* kfushimi@eng.hokudai.ac.jp (K. Fushimi).

Fig. 1. Numerically calculated current and current density as a function of polarisation time when a disk electrode with a diameter of $10\,\mu m$ (solid line) and a rectangular electrode with a square of $500\,\mu m$ (dashed line) were polarised in a mass-transfer process. Diffusion coefficient was $6.5 \times 10^{-10}\,m^2\,s^{-1}$.

an electroactive species on the electrode. Fick's 2nd law gives the following diffusion equation:

$$\frac{\partial c}{\partial t} = D\nabla^2 c \tag{1}$$

where c and D are concentration and diffusion coefficient of the electroactive species, respectively. Laplacian ∇^2 for the general electrode is expressed for a linear diffusion field in a perpendicular direction z to the surface as follows.

$$\nabla^2 = \frac{\partial^2}{\partial z^2} \tag{2}$$

In the case of a small disk electrode, the diffusion field not only in the perpendicular direction but also in the radial direction r becomes important due to the geometric aspect of the electrode.

$$\nabla^2 = \frac{\partial^2}{\partial z^2} + \frac{\partial}{r\partial r} + \frac{\partial^2}{\partial r^2} \tag{3}$$

On the other hand, there is no difference in a non-Faradaic process, i.e., charging of a double layer, and electron transfer process between the microelectrode and the general electrode [13,14].

Current in the mass-transfer process flowing the disk electrode can be elucidated from the integration of concentration gradients at the electrolyte/electrode interface.

$$I = 2\pi nFD \int \left(\frac{\partial c}{\partial z}\right)_{z=0} rdr \tag{4}$$

Fig. 1 shows the current flowing through a micro-disk electrode or macro-square electrode obtained from numerical calculations using Eqs. (1)–(4). Although the absolute value of microelectrode current is significantly smaller, the relative value of microelectrode current normalised by electrode area, i.e., current density, is clearly larger than that of the macroelectrode. The microelectrode current attains a steady state more rapidly than does the macroelectrode current. The significant difference is caused by the shape and size of the diffusion layer formed on the electrode. A very small semi-spherical layer can be formed rapidly. The concentration gradient at the microelectrode edge is significantly high compared with that at the centre and the current flowing through the microelectrode becomes proportional to the edge length rather than electrode area. Furthermore, the diffusion layer on the microelectrode corresponds to the sensitive region of the electrode. This is one reason why the microelectrode used in SECM has high spatial sensitivity. In the case of an MCC, the diameter of the electrode is less than one hundred micrometres like an SECM probe. However, when diffusion in the radial direction is limited by an inside wall
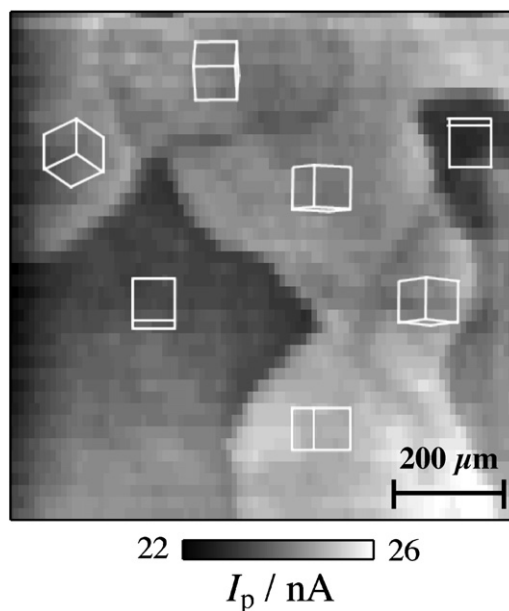

Fig. 2. SECM current image of an iron electrode passivated at 1.0 V (SHE) for 3.6 ks in deaerated pH 8.4 boric-borate buffer solution. For the SECM imaging, the specimen electrode and probe electrode, which was a platinum micro-disk electrode with a diameter of $10\,\mu m$, were polarised at 0.1 and 1.2 V (SHE), respectively, in $0.03\,mol\,dm^{-3}\,K_4[Fe(CN)_6]$ + pH 8.4 boric-borate buffer solution. The inter-electrode distance was kept at $5\,\mu m$ while the probe was scanned at $0.01\,\mu m\,step^{-1}$ in the x direction and $0.1\,\mu m\,step^{-1}$ in the y direction. The orientation was identified using an etch-pit method [15].

of the masking material, the mass-transfer process becomes more similar to that of a macroelectrode than that of a microelectrode.

3. Scanning electrochemical microscopy

Scanning electrochemical microscopy (SECM) was invented by Bard and et al. a quarter century ago. The basic principles of SECM have already been reported [6,7] and reviewed [15]. In SECM, the microelectrode is located in the vicinity of the specimen surface and used as an amperometric sensor in general. The diffusion layer on the microelectrode is deformed due to the electrochemical reactivity of the surface as well as the spatial limitation between the microelectrode and specimen surfaces. There are several SECM modes due to the polarisation manner of the specimen. The electrode potential of the specimen is free from an external control in the so-called feedback mode whereas it is controlled in the so-called generation/collection (G/C) mode. Furthermore, the G/C mode is classified into the substrate generation/tip collection (SG/TC) mode, in which products from the specimen is detected at the microelectrode, and the tip generation/substrate collection (TG/SC) mode, in which products from the microelectrode is reacted on the specimen electrode. In any modes, the scanning microelectrode allows to visualise the electrochemical activity image of the specimen interface. SECM is frequently used for electrochemistry of a liquid/liquid interface, biochemistry, and materials surface science. In the field of corrosion research, SECM is used to visualise a non-uniform surface reaction or to modify a surface selectively.

The passive film formed on iron shows an n-type semiconductive property [1] and the film thickness increases linearly with increasing formation potential [1,16]. Though the uniformity of film might play an important role for the passivation, it has not understood so well. Fig. 2 is a TG/SC mode SECM image of a passivated iron surface using a platinum microdisk electrode with a diameter of $10\,\mu m$ when the specimen and probe electrodes were polarised