Passive films formed on single grains of a polycrystalline pure iron substrate were investigated in 0.05 mol dm$^{-3}$ sulfuric acid with a micro-capillary cell (MCC). Passivation behavior under the condition of potentiostatic polarization was strongly dependent on the crystallographic orientation of the substrate surface. Electrochemical impedance spectroscopy revealed that the charge transfer resistance of the passivated surface was determined by the substrate orientation. Galvanostatic reduction and XPS analysis of the surface passivated using the MCC showed that the substrate orientation affected the chemical state of iron in the oxide. The results suggested that the aging of the passive film formed on the iron substrate depended on its crystallographic orientation due to the differences in surface energy of the substrate surface that has a bcc lattice structure. It was concluded that the grain dependency on the electric property of the passive film arose from the compositional differences of the oxide film.

In this study, grain-dependent passivation of iron single grains in sulfuric acid was investigated by using a micro-capillary cell (MCC) method in order to reveal how the surface orientation determines passive film formation.

### Experimental

**Sample preparation.** A polycrystalline iron plate with a purity of 99.99% annealed in vacuum of 2 × 10$^{-2}$ Pa at 1253 K for 7.2 ks for grain coarsening was used as a sample. The sample surface was ground with #400—4000 SiC papers and etched in 10 vol% HNO$_3$ solution for 10 s in order to remove the grinding affected layer. Then the surface was finished with mirror-like polishing by colloidal silica particles with a diameter of 0.04 μm to obtain a flat and smooth plane required for EBSD patterning. The texture of the sample surface was characterized by EBSD (SC-200, TSL) incorporated in a field emission auger microscope (JAMP-9500F, JEOL). Single grains for which crystallographic orientation could be approximated to {0 0 1}, {1 0 0}, and {1 1 1} planes within an Euler angle disparity of 10° were used for micro-electrochemical measurements with an MCC.

### Micro-electrochemistry

Micro-electrochemical measurements were carried out by using an MCC combined with a polarized microscope.$^{25,29}$ Figure 1 shows a block diagram of the MCC setup. A capillary tip was made of a PYREX glass capillary with an inner diameter of 3 mm and an outer diameter of 5 mm. After heating, pulling and grinding the glass capillary, a silicone sealant (RTV 118, Momentive) was glued to the sharpened tip of the capillary as a gasket ring. We prepared two capillary tips with inner diameters of 70 and 250 μm that achieved electrolyte contact areas of 3.7 × 10$^{-9}$ and 5.1 × 10$^{-8}$ m$^2$ on the sample surface, respectively. A LabVIEW (National Instruments) program was employed for controlling the XYZ-axis stage (TSDM40-15 and SGS40-5Z, Sigma Koki) and a force sensor (KD24S, ME-Meßsysteme) in order to put the capillary onto the single grains at a constant load. An Ag/AgCl/saturated KCl microelectrode (SSE) and a platinum wire were located in the capillary with a reversible hydrogen electrode (RHE) potential. The inside of the capillary was filled with an electrolyte of 0.05 mol dm$^{-3}$ H$_2$SO$_4$ aqueous solution (pH 1.3) deaerated by bubbling of pure Ar gas before the measurement. An FAS2 Femtostat (Gamry Instruments) was used for electrochemistry with the MCC.

After corrosion potential $E_{corr}$ measurement for 300 s, potentiodynamic polarization was performed from ($E_{corr}$ − 0.1 V) to 1.8 V (RHE) at a potential sweep rate of 5 mV s$^{-1}$. On a fresh sample surface, potentiostatic polarization at 1.2 V (RHE) for 3.6 ks was carried out and the current transient was recorded. Immediately after the
potentiostatic polarization, electrochemical impedance spectroscopy (EIS) was performed at 1.2 V (RHE) with an ac voltage amplitude of 10 mV in a frequency range from $10^3$ to $10^{-2}$ Hz. Curve fitting of impedance spectra was done by using a suitable equivalent electronic circuit (EEC) with Echem Analyst software (Gamry Instruments). Furthermore, after the potentiostatic polarization at 1.2 V (RHE), EIS for Mott-Schottky (MS) analysis was conducted in a potential range from 1.2 to 0.5 V (RHE) with an ac voltage amplitude of 10 mV at the frequency of 100 Hz. Separately, the sample polarized at 1.2 V (RHE) from 1.2 to 0.5 V (RHE) with an ac voltage amplitude of 10 mV at the frequency of 100 Hz. Separately, the sample polarized at 1.2 V (RHE) for 3.6 ks was galvanostatically reduced at the frequency of 100 Hz. Furthermore, after the potentiostatic polarization at 1.2 V (RHE), EIS circuit (EEC) with Echem Analyst software (Gamry Instruments).

X-ray photoelectron spectroscopy (XPS).—After potentiostatic polarization with the MCC, the samples were immediately rinsed with ethanol and dried with clean air. The composition of the polarized sample surface was studied by X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectra were recorded using a JPS-9200 photoelectron spectrometer (JEOL) with Al Kα radiation operating at 100 W (10 kV, 10 mA). This photoelectron spectrometer can analyze a micro-region by adjusting the angle-limiting aperture and the field view aperture, which select photoelectrons captured into the electrostatic lens and the analyzer, instead of focusing the X-ray. Here, we confined the detection area of photoelectrons to 200 μm in diameter by adjusting the two apertures to analyze the small sample area polarized with the MCC. Each sample area on the single grains was placed at the middle of the analyzing spot, observing the sample position with an optical microscope equipped on the spectrometer. The acquisition of each spectrum was repeated 100 times due to the small photoelectron intensity obtained from the small detection area. In this study, no sputtering to remove contamination on the surface was carried out to avoid reduction of oxidized iron species.32 Photoelectron deconvolution was performed to analyze the small detection area. In this sense, it is considered that the thick and wide silicon gasket rubber makes a tiny space between the rubber and the sample surface in the MCC. In the tiny space, diffusion of ferrous ions generated from the sample surface to the bulk electrolyte in an air-conditioned room at 295 K.

Results

Corrosion potential and dynamic polarization.—Figure 2 shows dynamic polarization curves measured on an iron {1 1 1} single grain at a potential sweep rate of 5 mV s$^{-1}$ following $E_{corr}$ measurement. The polarization curves show active, passive and trans-passive states of iron. The shape of the curve in this study resembled that in a previous work.33 In the passive state, a very stable passivity-maintaining current density less than 5 $\mu$A cm$^{-2}$ was assumed to be pixels belonging to a single grain. The mean grain size of the whole sample surface was ca. 500 μm. Relatively large single grains with lower Miller indexes of {0 0 1}, {1 0 1} and {1 1 1} were used as sample electrodes for the following polarizations with the MCC.

Since the diameter of the MCC was smaller than single grains on the sample, we could set a micro-electrode on a single grain. Just after installation of the MCC, the sample surface showed a relatively noble rest potential. However, it shifted immediately to a steady-state value of $E_{corr}$, suggesting that a native oxide film formed on the sample was removed due to acidity of the electrolyte. Figure 3a shows dynamic polarization curves measured on an iron {1 1 1} single grain at a potential sweep rate of 5 mV s$^{-1}$ following $E_{corr}$ measurement. The polarization curves show active, passive and trans-passive states of iron. The shape of the curve in this study resembled that in a previous work.33 In the passive state, a very stable passivity-maintaining current density of ca. $10^{-4}$ A cm$^{-2}$ flowed in this work, whereas current fluctuation was observed in the potential region from 0.65 to 1.30 V (RHE) in the previous work. In the active state, steady-state current density in this work was about twice that in the previous study, while similar currents flow in the passive state.

Figures 3b and 3c are optical images of the capillary tips that were used for potentiodynamic polarizations in this work and the previous work, respectively. The tips had the same inner diameters of 70 μm but different outer diameters and widths of the silicone rubber. When the capillary tip with a thin and narrow silicone gasket (Fig. 3b) was used for the MCC polarization, a number of facets that formed over the whole electrode surface were observed with SEM depending on the substrate orientation. The facets formed appear as a dark part in a micrograph (Fig. 3d). When the capillary tip with a thick and wide gasket (Fig. 3c) was used, on the other hand, the morphology of the polarized sample surface was inhomogeneous. The outside of the sample surface, which was laid under the gasket during polarization, dissolved but showed no facets (Fig. 3e).

It is obvious that the shape of the polarization curve depends on the geometry of the MCC. Localized concentration of dissolved iron species at the solution/electrode interface induces precipitation of iron oxide or iron hydroxide and acidification of the solution simultaneously, resulting in current oscillations in the active to passive transition.35 In this sense, it is considered that the thick and wide silicone gasket rubber makes a tiny space between the rubber and the sample surface in the MCC. In the tiny space, diffusion of ferrous ions generated from the sample surface to the bulk electrolyte in an air-conditioned room at 295 K.

Figure 1. Schematic setup of the micro-capillary cell (MCC).

Figure 2. Inverse pole figure (IPF) and EBSD IPF map of the iron sample surface.
active state was limited and the ions were highly concentrated. This results in a decrease in local pH due to hydrolysis by the formation of iron hydroxides, leading to destabilization of passivity. A smaller steady current in the active state in the previous study suggested that the diffusion of dissolved species is partially limited. These results indicate that the geometry of an MCC greatly affects electrochemical behavior of local surfaces.

During polarization in acidic media, the surface condition of an electrode is altered chemically and electrochemically. Under the condition of potentiodynamic polarization, the electrochemical behavior of the electrode surface significantly suffers from the previous polarization. In this sense, the iron species generated in an active state affect the behavior in a passive state. The MCC is much more susceptible than macro-electrochemical cells to dissolved species due to its small solution volume. Although there are some qualitative grain dependencies on polarization curves such as current fluctuation in a passive state, it is thought that the potentiodynamic polarization curve obtained by using the MCC is less suitable for detailed quantitative investigation of grain-dependent passivity.

**Potentiostatic polarization.**— Figure 4 shows a double logarithmic plot for current-time transients of three single grains during potentiostatic polarization at 1.2 V (RHE) in 0.05 mol dm$^{-3}$ sulfuric acid. In the initial period of polarization, an anodic current of ca. 0.2 A cm$^{-2}$ that is independent of the substrate orientation flowed due to charging of the double layer and subsequent active dissolution of the iron surface. The independence of the charging current for all grains indicates that the single grain samples had the same actual electrode area. The faradaic current started to decrease dramatically in a short period $t_p$ of a few seconds, corresponding to the commencement of oxide formation on the surface. The sequence of $t_p$ on single grains is in the order of \{1 1 1\} > \{1 0 1\} > \{0 0 1\}. This order is the same as that of the surface atom densities of body-centered cubic (bcc) iron, which are $1.88 \times 10^{-15}$, $1.73 \times 10^{-15}$ and $1.22 \times 10^{-15}$ cm$^{-2}$ for \{1 1 1\}, \{1 0 1\} and \{0 0 1\} planes, respectively. The total electric charge density $q_t$ consumed during the polarization for 3.6 ks depended on the orientation associated with $t_p$ (Table I). The values of $q_t$ are quite small compared with the charge density of ca. 17 C cm$^{-2}$ consumed in an active state under potentiodynamic polarization at 5 mV s$^{-1}$ (Fig. 3a), suggesting that the amount of dissolved species in the active state under potentiostatic polarization is very small. After polarization for ca. 10 s, the current decreased exponentially against polarization time with a slope $-d \log j / d \log t$ of ca. 0.65. The decrease in current was caused by the formation of an insulating oxide on the substrate. However, it competes with oxide film dissolution and/or substrate dissolution through the film since the slope is not unity like film formation in a high field mechanism in which the dissolution is negligible. While the \{1 0 1\} grain maintained a constant slope until 3.6 ks, the slopes on the \{0 0 1\} and \{1 1 1\} grains gradually decreased after 500 s. The slope on the \{0 0 1\} grain became almost zero after 3 ks. Therefore, the current density $j_t$ at 3.6 ks was strongly dependent on the substrate orientation (Table I), although the values of $j_t$ are in the order of \{0 0 1\} > \{1 1 1\} > \{1 0 1\}, which is a different sequence from $t_p$. This suggests that the three single grains exhibited different activities in the initial formation and the following aging of the oxide film.

![Figure 3](image1.png)

**Figure 3.** (a) Anodic polarization curves of an iron \{1 1 1\} single grain in 0.05 mol dm$^{-3}$ sulfuric acid measured by using the latest and previous MCCs. The potential was swept at 5 mV s$^{-1}$. Optical microscopic images of (b, c) capillary tips and (d, e) sample surfaces after MCC polarization in (b, d) this investigation of grain-dependent passivity.

![Figure 4](image2.png)

**Figure 4.** Double logarithmic plots of current-time transients of iron \{0 0 1\}, \{1 0 1\} and \{1 1 1\} single grains under the condition of potentiostatic polarization in 0.05 mol dm$^{-3}$ sulfuric acid at 1.2 V (RHE) for 3.6 ks.

| Surface | $t_p$ (s) | $q_t$ (C cm$^{-2}$) | $j_t$ ($10^{-6}$ A cm$^{-2}$) |
|---------|---------|-----------------|-----------------|
| \{0 0 1\} | 3.7 ± 1.5 | 0.54 ± 0.33 | 2.9 ± 0.50 |
| \{1 1 1\} | 5.2 ± 1.1 | 1.2 ± 0.11 | 1.9 ± 0.21 |
| \{1 0 1\} | 4.6 ± 1.2 | 0.85 ± 0.38 | 1.3 ± 0.12 |

Table I. Experimental parameters of potentiostatic polarization at 1.2 V (RHE) for 3.6 ks in 0.05 mol dm$^{-3}$ sulfuric acid, $t_p$, passivating time; $q_t$, total charge density consumed for 3.6 ks; $j_t$, current density at 3.6 ks.
Electrochemical impedance spectroscopy (EIS).— Under the condition of the potentiostatic polarization for 3.6 ks in 0.05 mol dm$^{-3}$ sulfuric acid, about 5% of the $i_t$ decreased during the last 500 s. During this period, it was considered that the formation and dissolution of the oxide film were almost in a steady-state and that the film property was not changed significantly. Although the measurement period of 460 s was necessary to take an impedance spectrum, immediately after the potentiostatic polarization with the MCC, EIS was carried out on single grains to investigate the electric property of the electrode surface polarized at 1.2 V (RHE). In a Bode plot (Fig. 5), the three grains show almost the same shapes in the whole frequency range. The phase shift $\theta$ determined by the capacity reactance of the oxide film shows a single peak at ca. 50 Hz. However, the impedance amplitude $|Z|$ depends on the grain orientation at frequencies lower than 0.1 Hz, and the value of $|Z|$ on the {1 0 1} grain is the largest among the three grains. In a Nyquist plot, a single capacitive semicircle was observed for all grains. The diameter of the semicircle significantly depended on the substrate orientation and showed the sequence of {1 0 1} > {1 1 1} > {0 0 1}. Since no other semicircles were observed in the higher frequency region in the Nyquist plot, the electrode process can be described by a single time constant and an electrode interface can be represented by a so-called Randles type EEC shown in Fig. 6, where $R_{el}$ and $R_{ct}$ are electrolyte and charge transfer resistances, respectively, and CPE is a constant phase element. Since the impedance spectra were measured at the film formation potential, $R_{el}$ includes ionic and electronic resistances corresponding to the film formation and dissolution. The CPE can be substituted with the interfacial capacitance $C$ as follows:

$$ C = Q^{\alpha} (R_{el}^{-1} + R_{ct}^{-1})^{(\alpha-1)/\alpha}, \quad [1] $$

where $Q$ and $\alpha$ are the CPE constant and coefficient, respectively. Curve fitting of the impedance spectra with the EEC revealed that the values of $R_{el}$ were $42.9 \pm 6.6, 69.2 \pm 6.2$ and $107.3 \pm 11.0 \Omega \cdot \text{cm}^2$ for the {0 0 1}, {1 1 1} and {1 0 1} grains, respectively, while the $C$ values of the three grains were about 11.3 $\mu\text{F} \cdot \text{cm}^{-2}$. The smaller difference in $C$ means that the thickness of the oxide film formed on each grain was almost constant. The grain dependency on $R_{el}$ is remarkable and the {1 0 1} grain showed a 2.5-times larger value of $R_{el}$ than that of the {0 0 1} grain. However, the values of $R_{ct}$ were less than half that (210 $k\Omega \cdot \text{cm}^2$) of a passive film formed on iron in neutral borate solution. $\text{It is thought that the lower solution pH leads to greater reactivity for a charge transfer reaction such as film dissolution.}$

The MS equation for an n-type semiconductor is

$$ C_{SC} = \frac{2}{\varepsilon N_0} (E - E_{fb} - kT/e), \quad [2] $$

where $C_{SC}$ is the space charge layer capacitance, $\varepsilon$ is the electron charge, $N_0$ is the donor density, $\varepsilon$ is the dielectric constant of the semiconductor, $e_0$ is the permittivity in vacuum, $E_{fb}$ is the flatband potential, $k$ is the Boltzmann constant and $T$ is the absolute temperature. The value of $C_{SC}$ is derived from the interfacial capacitance $C$ and the Helmholtz layer capacitance $C_H$:

$$ C = (C_{SC}^{-1} + C_H^{-1})^{-1}. \quad [3] $$

The $C_H$ values of $2.3 - 2.5 \mu\text{F} \cdot \text{cm}^{-2}$ were reported for iron electrode in sulfuric acid. Assuming $C_{H} = 2.3 \mu\text{F} \cdot \text{cm}^{-2}$, the $C_{SC}$ value was similar with the measured value $C$ within the difference of less than 1%. Thus, the value of $C$ can be regarded as $C_{SC}$ in this study.

It is well known that an oxide film formed on an iron surface displays an n-type semiconductor property. Azumi et al. reported that the values of $E_{fb}$ and $N_0$ of passive films formed on iron in pH 6.5 borate or phosphate solutions at 1.2 V (RHE) were ca. 0.5 V (RHE) and 6 - 10 $\times 10^{20} \text{cm}^{-3}$, respectively. MS analysis with the MCC was conducted for the passive oxide film formed on the single grain. Figure 7a shows MS plots of {0 0 1}, {1 0 1} and {1 1 1} grains polarized at 1.2 V (RHE) for 3.6 ks in 0.05 mol dm$^{-3}$ sulfuric acid with the values of $C_{SC}$ were measured at the frequency of 100 Hz. A linear relationship between $C_{SC}^{-2}$ and potential $E$ can be found at a potential range from 0.8 to 0.6 V (RHE). Extrapolation of the relationship shows $E_{fb}$ values of ca. 0.46 V (RHE) in the order of...
\{1\,0\,1\} > \{0\,0\,1\} > \{1\,1\,1\} \) with ca. 20 mV intervals, while \(N_D\) values of 4.7–5.3 \times 10^{20} \text{ cm}^{-3} \) for the three grains were calculated from the slope assuming \(t = 40\) \text{s}. \(^{38}\) The values are similar to those reported for polycrystalline iron as described above. However, the \(N_D\) values are slightly larger than that of a passive film formed in a neutral borate solution,\(^ {44,46}\) suggesting that reduction of the oxide film was a cathodic current in a potential region from 0.9 to 0.53 V (RHE) which is a potential change rate similar to that in the MS analysis, in immediately after potentiostatic polarization at 1.2 V (RHE) for 3.6 ks in 0.05 mol dm\(^{-3}\) sulfuric acid. Figure 8 shows changes in electrode potential when \(\{0\,0\,1\}, \{1\,0\,1\} \) and \(\{1\,1\,1\}\) single grains were galvanostatically reduced at \(-6 \mu\text{A cm}^{-2}\) using the MCC. Initially, the potential declined steeply from ca. 1.0 V (RHE) and reached a plateau potential at ca. 0.6 V (RHE). Subsequently, the potential dropped in parallel with the electrochemical reactions of Eq.4 and/or 6 in a lower Miller indexes under the condition of potentiostatic polarization with the MCC had more defects, which behaved as donors for charge transfer, than those of a passive film formed in a neutral solution. On the other hand, potentiodynamic polarization in the cathodic direction was conducted at a potential sweep rate of \(-10 \text{ mV s}^{-1}\), which is a potential change rate similar to that in the MS analysis, in 0.05 mol dm\(^{-3}\) sulfuric acid with the MCC after potentiostatic polarization at 1.2 V (RHE) for 3.6 ks. The whole sample surface allowed a cathodic current in a potential region from 0.9 to 0.53 V (RHE) as shown in Fig. 7b, suggesting that reduction of the oxide film was possible during the MS analysis. In this potential region, a relatively large scattering of standard deviation is observed in the MS plot. Although the values of \(E_0\) and \(N_D\) show some grain dependencies, the reliability of MS analysis in this experiment is not superior. In order to evaluate the grain dependency in the semiconductor properties of oxide films more precisely, MS analysis under milder conditions in which no reduction of the oxide film occurs might be necessary.

**Galvanostatic reduction of the passive film.**— Separately from EIS, cathodic reduction of the passive oxide film was performed immediately after potentiostatic polarization at 1.2 V (RHE) for 3.6 ks in 0.05 mol dm\(^{-3}\) sulfuric acid. Figure 8 shows changes in electrode potential when \(\{0\,0\,1\}, \{1\,0\,1\} \) and \(\{1\,1\,1\}\) single grains were galvanostatically reduced at \(-6 \mu\text{A cm}^{-2}\) using the MCC. Initially, the potential declined steeply from ca. 1.0 V (RHE) and reached a plateau potential at ca. 0.6 V (RHE). Subsequently, the potential dropped to estimate quantitatively the amount of Fe\(_2\)O\(_3\) in the film from the following reaction occurs:

\[ \text{Fe}_2\text{O}_3 + 6\text{H}^+ + 2e^- = 2\text{Fe}^{2+} + 3\text{H}_2\text{O} \]  

(4)

at potentials less than

\[ E^\circ(\text{RHE}) = 0.569 - 0.0591 \log[\text{Fe}^{2+}] \]  

(5)

When the electrode covered with Fe\(_2\)O\(_3\) is at the potential of 1.0 V (RHE) or 0.6 V (RHE), the concentration of ferrous ions [Fe\(^{2+}\)] at an electrode interface is equal to \(5.1 \times 10^{-8} \text{ mol dm}^{-3}\) or \(3.0 \times 10^{-11} \text{ mol dm}^{-3}\), respectively. Ferrous ions in the solution are derived from the substrate iron during potentiostatic and galvanostatic polarizations. Therefore, changes in electrode potential during the reduction indicate that the electrolyte solution was not so highly concentrated with ferrous ions at the end of the potentiostatic polarization, although [Fe\(^{2+}\)] at the oxide/solution interface increased during the galvanostatic polarization.

Obloensky et al.\(^ {48}\) explained on the basis of results of an in situ XANES study that the plateau potential under galvanostatic reduction of the passive film formed on iron in acetate buffer represented the simultaneous reduction of Fe\(_2\)O\(_3\) to Fe\(_3\)O\(_4\) and Fe\(^{2+}\) as follows:

\[ 2\text{Fe}_2\text{O}_3 + 4\text{H}^+ + 2e^- = \text{Fe}_3\text{O}_4 + 2\text{Fe}^{2+} + 2\text{H}_2\text{O} \]  

(6)

Fe\(_2\)O\(_3\) dissolves chemically in an acidic solution.\(^ {47}\) When the substrate iron is partially exposed to the solution, the remaining oxide (including Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\)) seems to be removed rapidly since an electrochemical dissolution of the substrate Fe can drive an electrochemical reduction of the oxide. As a result, the potential shifts immediately to another plateau where hydrogen evolution reaction on the substrate iron is dominant.

It is thought that the order of \(q_i\) corresponds to the grain dependency on the amount of Fe\(_2\)O\(_3\) in the film. From Eq. 6, a charge density of 0.29 mC cm\(^{-2}\) was required to reduce Fe\(_2\)O\(_3\) with a thickness of 1 nm that was contained in the oxide film formed in an acidic solution.\(^ {31}\) The \(q_i\) values are less than that required to reduce all of the Fe\(_2\)O\(_3\). This indicates that a chemical dissolution of the oxide film proceeded in parallel with the electrochemical reactions of Eq. 4 and/or 6 in a low pH solution.\(^ {36}\) Thus, the chemical dissolution made it difficult to estimate quantitatively the amount of Fe\(_2\)O\(_3\) in the film from the galvanostatic polarization in this study.

**X-ray photoelectron spectroscopy.**— After potentiostatic polarization of a single grain with the MCC that has a tip diameter of ca. 250 \(\mu\text{m}\), XPS analysis of the polarized surface was conducted with a photoelectron detection diameter of 200 \(\mu\text{m}\). Figure 9 shows Fe 2p\(_{3/2}\) photoelectron spectra obtained from the surfaces of iron \(\{0\,0\,1\}, \{1\,0\,1\} \) and \(\{1\,1\,1\}\) single grains polarized at 1.2 V (RHE) for 3.6 ks in 0.05 mol dm\(^{-3}\) sulfuric acid. Although several deconvolution components for iron oxides have been reported for analyzing photoelectron spectra of passive oxide films on iron,\(^ {39-51}\) we focused on Fe\(^{3+}\) and Fe\(^{2+}\) ions for oxidized iron species in order to identify the grain dependency on the oxidation state of iron atoms in the passive film. The spectra after background subtraction were deconvoluted into three curves that represent different oxidation states of iron species, Fe\(^{3+}\), Fe\(^{2+}\) and Fe\(^{2+}\), using the XPS peak energies for the standards reported by Keller and Strehlow.\(^ {30}\) A relatively large peak of Fe\(^{2+}\) is observed, probably due to the position mismatch between the passivation and detection areas, and the spectrometer detected photoelectrons that came from outside the passivated area. Therefore, the intensity of Fe\(^{2+}\) should be excluded to discuss the grain dependency of the oxide film. The ratio Fe\(^{3+}/\text{Fe}^{2+}\) of peak intensity clearly depended on the orientation, being \(1.25 \pm 0.09, 2.14 \pm 0.19\) and \(3.82 \pm 0.36\) for the iron \(\{0\,0\,1\}, \{1\,1\,1\} \) and \(\{1\,0\,1\}\) single grains, respectively. This indicates that the film composition depended on the substrate orientation and that the relative quantity of Fe\(^{3+}\) in the film was larger in the order of \(\{1\,0\,1\} > \{1\,1\,1\} > \{0\,0\,1\}\).

**Discussion**

A protective surface restricts an anodic current and shows a high resistance for anodic charge transfer reactions. The highest charge transfer resistance on the \(\{1\,0\,1\}\) grain was confirmed by EIS as well as \(j_i\) in the potentiostatic polarization. Thus, the \(\{1\,0\,1\}\) grain was the most protective surface among the three single grains with lower Miller indexes under the condition of potentiostatic polarization in sulfuric acid. XPS analysis revealed that the oxide formed on the
\[ \text{Fe} \rightarrow \gamma\text{-Fe}_2\text{O}_3 \rightarrow 3\text{Fe}_3\text{O}_4 \quad \text{(7)} \]

where the \( \Delta G \) values of the formation of \( \text{Fe}_3\text{O}_4 \) and \( \gamma\text{-Fe}_2\text{O}_3 \) are \(-1014.88 \text{ kJ mol}^{-1}\) and \(-727.9 \text{ kJ mol}^{-1}\), respectively.\(^{56,57}\) On the other hand, the surface energy of a bcc lattice structure is greater in the order of \{0 0 1\} > \{1 1 1\} > \{1 0 1\}. It is reasonable that the \{1 0 1\} grain of bcc iron has a low activity for Eq. 7 and is impoverished in Fe\(^{3+}\) more than the other grains. Furthermore, the electric resistance \( \rho \) of bulk \( \text{Fe}_3\text{O}_4 \) is significantly smaller than that of \( \gamma\text{-Fe}_2\text{O}_3 \) \((\rho = 1 \times 10^{-3} \text{ \Omega m}^{\text{m}} \text{ and } 10^5-10^7 \text{ \Omega m}^{\text{m}} \text{ for } \text{Fe}_3\text{O}_4 \text{ and } \gamma\text{-Fe}_2\text{O}_3 \text{, respectively.})\) It is thought that the Fe\(^{3+}\)-impoverished oxide film on the \{1 0 1\} grain exhibits higher \( R_\theta \) than does that on the other grains.

If the oxide film formed on iron in sulfuric acid has a bi-layer structure, grain-dependent layer structures can be assumed as shown in Fig. 10. While both oxide films have similar thicknesses since the interfacial capacitance \( C \) is independent of substrate orientation, they show different ratios in thickness of an inner \( \text{Fe}_3\text{O}_4 \) layer and an outer \( \gamma\text{-Fe}_2\text{O}_3 \) layer. On the \{1 0 1\} grain, for which XPS analysis showed the largest \( \text{Fe}^{3+}/\text{Fe}^{2+} \) ratio among the three grains, the outer \( \gamma\text{-Fe}_2\text{O}_3 \) layer accounts for a larger proportion of the film than does that of the \{0 0 1\} grain. Hence, the \{1 0 1\} grain shows higher charge transfer resistance for the thinnest outer \( \gamma\text{-Fe}_2\text{O}_3 \) layer than do the other grains. Although the film structure of the iron \{1 1 1\} grain is not depicted in Fig. 10, it is thought that the ratio of \( \text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3 \) represents a value between those of the iron \{1 0 1\} and \{0 0 1\} grains.

The defect structure of an oxide film must be taken into account when we consider the electric property of an anodic oxide film that grows under a high electric field, where the charge transfer resistance involves not only electronic resistance but also ionic resistance. Greater ionic defects in the oxide film allow a larger ionic current, and oxide ions\(^{61}\) and/or alternative cations\(^{62}\) carry the ionic current in the anodic oxide film on iron. Davenport et al. conducted in situ surface XRD and suggested that the passive film formed on the iron \(0 0 1\) face was less defective than that formed on the iron \{1 0 1\} face due to the larger grain size and fewer antiphase boundaries of the oxide film on the \{1 0 1\} face.\(^{55}\) Their results indicate that the \{1 0 1\} grain shows a higher ionic resistance than that of the \{0 0 1\} grain. In this study, however, the \{1 0 1\} grain exhibited the largest charge transfer resistance. Thus, it can be assumed that the grain dependency on the electric property of the passive film on iron is greatly affected by electronic conduction of the oxide, which is caused by the generation of Fe\(^{3+}\) ions in the oxide and the continuous interchange of electrons between Fe\(^{3+}\) and Fe\(^{2+}\) ions.

As discussed above, crystallographic orientation of the surface affects both electronic and ionic currents through the anodic oxide film. Synergistic charge transfer resistance in the passive state was summarized as in the order of \{1 0 1\} > \{1 1 1\} > \{0 0 1\}. The substrate orientation also affects the film composition as well as concentration of defects of the film. MCC polarization of an EBSD-identified surface enables precise identification of the crystallographic orientation dependency of many single grains on polycrystalline iron. Expanding the measurements to grains with higher Miller indexes and grain boundaries may reveal the detailed mechanism and kinetics of grain selective corrosion that occurs on polycrystalline iron.

Conclusions

Grain-dependent passivation of iron single grains in sulfuric acid was investigated individually with an MCC. Under the condition of potentiostatic polarization, iron \{0 0 1\}, \{1 0 1\} and \{1 1 1\} single...
grains showed different passivation behavior, and the current density after polarization for 3.6 ks became larger in the order of \{0 \, 0 \, 1\} > \{1 \, 1 \, 1\} > \{1 \, 0 \, 0\}. EIS following the passivation revealed that the charge transfer resistance of the passive film formed on the iron single grains greatly depended on the substrate orientation and exhibited a larger value in the order of \{1 \, 0 \, 0\} > \{1 \, 1 \, 1\} > \{0 \, 0 \, 1\}. It was considered from galvanostatic reduction and XPS analysis that the structure of the passive film formed on iron depended on the substrate orientation due to the different surface energy of bcc iron. Considering that the structure of the oxide film formed in sulfuric acid was bilayered with an inner FeO layer and an outer γ-Fe₂O₃ layer, the ratio of these two oxide layers depended on the substrate orientation. The outer γ-Fe₂O₃ layer accounted for a large proportion of the film on the \{1 \, 0 \, 0\} grain, resulting in the highest charge transfer resistance among the three single grains. Our study also indicated that the grain dependency on the electric property of the oxide film on iron depends on the composition of the film rather than defect concentration.

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