For the establishment of a sustainable society, it is important to predict and prevent degradation of metal materials induced by corrosion. If the material has a homogeneous surface, corrosion degradation can be predicted by the assumption of homogeneous corrosion kinetics. In general, however, the surface of a metallic material is heterogeneous rather than homogeneous due to its composition, crystallographic orientation, and tendency to disorder. It is more difficult to estimate the corrosion degradation of a heterogeneous material than that of a homogeneous material. Dual-phase steel has a heterogeneous structure composed of ferrite and a second phase such as austenite or martensite. Because of their excellent ductility and formability, dual-phase steels play an important role in the automobile industry, and it is expected that the demand for such steels will increase in the future. However, it has been shown that one phase corrodes preferentially due to formation of a galvanic couple by contact to the other phase. In a reducing acid solution, selective corrosion of ferritic-austenitic duplex stainless steel occurs due to preferential attack on the ferrite phase. In general, the alloy composition (Cr, Ni, Mo, N, etc.) distributed to each phase has a drastic impact on the corrosion resistance of duplex stainless steel. However, the effect of the crystal structure of dual-phase steel on corrosion resistance is not so clear compared with the effect of chemical composition.

Several electrochemical methods for detailed investigation of the heterogeneous corrosion of dual-phase steel have been reported. One of the methods for investigating the corrosion behavior of each phase of dual-phase steel is the use of a single-phase electrode preparation. Lee et al. separated super duplex stainless steel into ferrite phase and austenite phase by selective dissolution and embedding with resin, and they evaluated the corrosion resistance of each phase. Although a single-phase electrode enables accurate measurement of the resistance of each phase, preparation of a separated specimen is complicated and sometimes difficult in cases in which one phase has a corrosion behavior similar to that of another phase. For investigation of heterogeneous corrosion, another effective method is microelectrochemistry. The micro-capillary cell technique and scanning electrochemical microscopy (SECM) enable analysis of the electrochemical behavior of a local surface with the intact environment. Muto et al. investigated the pitting corrosion mechanism of type-304 stainless steel derived from MnS inclusion dissolution using a micro-capillary cell. Microelectrochemical measurement revealed that accumulation of dissolution species from MnS inclusion affected the generation of metastable pits. Moreover, Takabatake and Fushimi reported that the corrosion behavior and passive film property of polycrystalline pure iron depended on the underlying crystallographic orientation. Scanning electrochemical microscopy (SECM) has often been used to study corrosion of metals in solution. Fushimi et al. investigated the reaction activity of iron, titanium, and FeAlC surfaces using SECM. They reported that differences of reaction activity in the active or passive state according to crystal grains were caused by crystallographic orientation and grain boundaries. Recently, Lombardia and co-workers studied the grain-dependent corrosion of copper using SECM and in situ electrochemical scanning tunneling microscopy (ECSTM). They reported that <111> oriented grains of copper are susceptible to corrosion in active state. Nevertheless, in passive state <111> surfaces are more protective compared with <001> surfaces. Scanning Kelvin probe force microscopy has also been applied to a duplex stainless steel surface and it was shown that the phase boundary between ferrite and austenite phases exhibited a lower potential in the ferrite phase. It is essential to use a microelectrochemical technique for distinction between corrosion behavior of the object to be measured and that of others with only a slight difference.

In our previous work, heterogeneous corrosion behavior of high-purity dual-phase carbon steel was investigated in sulfuric acid. The dual-phase carbon steel was composed of ferrite and martensite phases with almost constant carbon contents but no pearlite. It is revealed that the ferrite phase dissolved twice as fast as the martensite phase using a micro-capillary cell. Dual-phase carbon steel has the advantage of being able to exclude the impact of alloy elements, and it enables investigation of the corrosion behavior mainly depending on the crystal phase. For more information about heterogeneous corrosion, it is important to investigate the passive film properties. However, there are few reports about the properties of a passive film on dual-phase carbon steel. In this work, heterogeneous passivity of dual-phase carbon steel was investigated using microelectrochemical methods including SECM.

### Experimental

Carbon steel sheets of pure ferrite phase (100F), pure martensite phase (100M) and dual phase (50F50M) were prepared in the same manner as that reported previously. Optical microscopic images of the etched steels are shown in Figure 1. The 100F and 100M steels are clearly single phase whereas the 50F50M steel shows almost equal proportion of the two phases. Square steel pieces of 0.5 cm in size were used as specimen electrodes after embedding in epoxy resin (5071, Technovit) and mechanical polishing with colloidal silica particles of 0.04 μm in size (40700000, Struers). The electrolyte solution used was...
pH 8.4 boric acid-borate buffer (0.15 mol dm$^{-3}$ H$_3$BO$_3$ and 0.15 mol dm$^{-3}$ Na$_2$B$_4$O$_7$) deaerated by bubbling with pure argon gas. Most of the electrochemical measurements were carried out with a potentiostat (SP-150, BioLogic) and a conventional electrochemical cell with a platinum counter electrode and an Ag/AgCl/saturated KCl reference electrode with a Luggin-Haber capillary in an air-conditioned room at 295 K. All of the potentials were converted to standard hydrogen electrode (SHE) scale.

Dynamic polarization of a specimen was conducted just after the polishing at a potential sweep rate of 1 mV s$^{-1}$ in a potential range from 0.1 V more negative than the corrosion potential, $E_{\text{cor,AP}}$, to 1.3 V (SHE). Prior to investigation of the passivity of the specimen surface, the specimen electrodes were polarized potentiostatically at the film formation potential $E_i = 0.5, 0.7$ or 0.9 V (SHE) for 3600 s. Electrochemical impedance spectroscopy (EIS) of the passivated specimen was carried out at $E_i$ by superimposing an ac voltage of ±5 mV in a frequency range of $10^2$–$10^{-2}$ Hz. A software package (EC lab V, BioLogic) was used for curve fitting of the impedance data. Mott-Schottky analysis was also conducted to evaluate the semiconducting properties of the passive film formed on the specimen surface. Capacitance measurements were performed at a frequency of 10 Hz while the applied potential was stepwise shifted from the potential of $E_i$ to −0.2 V (SHE).

Redox activity imaging of the passivated specimen surface was conducted by SECM. The set-up of SECM was similar to that used previously. A microelectrode was prepared by sealing a platinum wire with a diameter of 10 μm into a glass capillary and by polishing the tip. The microelectrode and substrate electrode of 50F50M were connected to a bipotentiostat (HAL-1512 mM2, Hokuto Denko) and polarized potentiostatically at $E_i = 0.6$ V (SHE) and $E_f = 0.1$ V (SHE), respectively, in boric acid-borate buffer solution containing 1 mol m$^{-3}$ hydroxymethylferrocene (FcMeOH) as a redox mediator. With the distance between the microelectrode and substrate kept at 5 μm, the microelectrode was scanned above the 500 μm square substrate in a stepwise manner with increments of $dx = 4$ μm and $dy = 8$ μm and with intervals of 5 s and 0.5 s, respectively.

The thickness of the oxide film formed on the surface was measured by an ellipsometer (SE-101, Photonic Lattice) with optical constants of 3.180–3.850 i for the iron substrate and 2.550–0.350 i for the iron oxide film.

Results and Discussion

DC polarization behavior.— Fig. 2 shows dynamic polarization curves of 100F, 100M, and 50F50M steels. A cathodic current, which is mainly attributed to reduction of oxygen dissolved in the solution, flows at potentials below the $E_{\text{cor,AP}}$.

Table I shows the $E_{\text{cor,AP}}$ of steel specimens in pH 8.4 boric acid-borate buffer just after polishing. The $E_{\text{cor,AP}}$ of 50F50M steel is an intermediate value of those of 100F pure martensitic steel and 100F pure ferritic steel. The $E_{\text{cor,AP}}$ increases as the volume fraction of ferrite increases, i.e., 100M < 50F50M < 100F.

At potentials higher than the $E_{\text{cor,AP}}$, the anodic current increases monotonously and reaches a passivity-maintaining current. No anodic current peak is observed before the steady state, suggesting that the specimen surface was spontaneously passive. This is due to exposure of the specimen surface to air for a few minutes needed for introduction into the cell after polishing and to formation of an air-oxidized film covering the surface. In general, the passivity of iron is characterized after removal of the surface oxide by galvanostatic reduction.

Table I also shows corrosion potentials $E_{\text{cor,GR}}$ after a galvanostatic reduction at −20 μA cm$^{-2}$ for 300 s of carbon steels. The values of $E_{\text{cor,GR}}$ are several hundred millivolts lower than the $E_{\text{cor,AP}}$. The sequence of $E_{\text{cor,GR}}$ is inverse to that of $E_{\text{cor,AP}}$ but similar to that measured in sulfuric acid. The lower $E_{\text{cor,GR}}$ of 100M compared with that of 100F indicates that the air-oxidized film on the martensite phase is a relatively stable. Additionally, the corrosion current density of 100M is larger than that of 100F. There is no doubt that the reactivity of the martensite phase surface is higher than that of the ferrite.

Table 1. Corrosion potential after polishing ($E_{\text{cor,AP}}$) and corrosion potential after galvanostatic reduction ($E_{\text{cor,GR}}$) of steels.

| Specimen | 100F | 50F50M | 100M |
|----------|------|--------|------|
| $E_{\text{cor,AP}}$ (SHE) / V | −0.089 | −0.124 | −0.189 |
| $E_{\text{cor,GR}}$ (SHE) / V | −0.528 | −0.468 | −0.406 |
phase surface. This can probably be attributed to the high surface energy on the disordered surface structure of martensite phase. The large passivity-maintaining current density of 100M means that not only the air-oxidized film but also the anodic oxide film formed on 100M has a larger electric and/or ionic conductivity than those of 100F. After galvanostatic reduction, in any case, dynamic polarization showed a current peak attributed to active dissolution. In the following measurements, galvanic reduction treatment was not conducted to prevent penetration of hydrogen into the steel surface arising from the hydrogen evolution reaction.

Fig. 3 shows representative current transients of the steel specimens during potentiostatic polarization at 0.9 V (SHE). The initial current density just after the polarization is associated with charging of the electric double layer on the specimens. It shows no difference depending on the specimen, indicating that the specimens have the same surface area. Current density decreases exponentially. During polarization for 10 s, the plot shows a linear relationship with a slope of -1, suggesting that the oxide film forms on the surface by a high field mechanism.26 However, current densities of the specimens are slightly different. The current density of 100M is larger than those of 50F50M and 100F. After polarization for 100 s, the slopes of 50F50M and 100M become gentler. It is thought that a conductive film is formed on the martensitic substrate. In the plot of 100F after 100 s, there are several noise-like spikes because of the small current. After 1000 s, the current approaches a steady-state value. The current density at 3600 s shows a sequence of 100F (1.1 μA cm⁻²) < 50F50M (1.5 μA cm⁻²) < 100M (2.1 μA cm⁻²). This means that the passive film formed on martensite has high electric and/or ionic conductivity. Charges consumed during potentiostatic polarization for 1 to 1000 s of 100F, 50F50M and 100M were 2.2, 3.4 and 5.0 mC cm⁻², respectively. Iron oxide is very stable in pH 8.4 solution because it does not dissolve into metal cations. Assuming that the oxide formed on the specimen surface is Fe₂O₃ and is proportional to the consumed charges, thicknesses are estimated from Faraday’s law to be 3.4 and 7.9 nm on 100F and 100M, respectively. These are in good agreement with the thicknesses, 4.5 and 8.0 nm for 100F and 100M, respectively, measured by ellipsometry after film formation in air. It is thought that martensite phase allows formation of a two-times larger amount of anodic oxide film than dose ferrite phase. A relatively thick oxide film with more defects seems to be formed on the martensite phase.

EIS.— Fig. 4 shows a Bode plot of the steels following the formation of a passive film by potentiostatic polarization at Eᵢ. Since one time constant is observed in the spectrum, the plot is fitted with a so-called Randles-type RC-R electric circuit. Although a constant phase element (CPE) provides better curve fitting, capacitance C was used because the CPE coefficient was close to 1.

Figs. 5a and 5b show charge transfer resistance Rₜ and C, respectively, as a function of Eᵢ. The value of Rₜ is almost independent of Eᵢ, although 100F shows 3.5 to 4-times larger values of Rₜ than those of 100M. In contrast, the value of C decreases with increase in Eᵢ, although the line slopes are dependent on the specimens. C of 100M was 1.4-times larger than that of 100F at 0.5 V (SHE), while the difference is very small at 0.9 V (SHE). C is consisted of film capacitance Cᵢ and Helmholtz layer capacitance C_H (~20 μF cm⁻²) as follows:

\[ \frac{1}{C} = \frac{1}{C_i} + \frac{1}{C_H} \]  

The relatively large capacitance of 100M at Eᵢ = 0.5 V (SHE) may be due to the large actual surface area. When the passive film is regarded as a parallel capacitor, thickness of the space charge layer d_sc in the film is inversely proportional to Cᵢ:²⁷

\[ d_{SC} = \frac{ε_0 ε}{C_i} \]  

where ε and ε₀ are relative permittivity (ε = 40)²⁸ and permittivity in vacuum, respectively. Thus, the calculated values of d_sc are 1.3 nm and 0.6 nm for 100F and 100M, respectively. d_sc of 100M is two-times smaller than that of 100F. The small passivity-maintaining current and Rₜ suggested that a defective passive film tends to form on the martensite phase.

The passive film formed on iron shows an n-type semiconducting property, and the Mott-Schottky equation of an n-type semiconductor
is expressed as follows: \[ \frac{1}{C^2} = \left( \frac{2}{\varepsilon N_D e_0} \right) \left( E - E_{fb} - \frac{kT}{e} \right). \] where \( e \) is the elementary charge, \( N_D \) is donor density, \( e_0 \) and \( \varepsilon \) are permittivity in vacuum and relative permittivity, respectively, \( E_{fb} \) is flatband potential, \( k \) is Boltzmann constant and \( T \) is absolute temperature. Fig. 6 shows a Mott-Schottky plot of the passivated steels. It is clear that the oxide films formed on the steels have an n-type semiconductors depends on grain boundary length or misorientation angle.30 and co-workers reported that the value of carrier density of semiconductors increases with increasing substrate crystallographic orientation. Good agreement for the results of a previous study15 showing that \( E_{fb} \) is independent of the substrate, being in agreement with the results of a previous study15 showing that \( E_{fb} \) is not affected by substrate crystallographic orientation. Good agreement for \( E_{fb} \) suggests that there is little difference in chemical composition of the passive films on the specimens. On the other hand, the value of \( N_D \) obtained from the slope in the plot strongly depends on the substrate structure and decreases with increase in \( E_{fb} \). \( N_D \) values of 50F50M and 100M are larger than that of 100F. It is clear that \( N_D \) of the oxide is correlated with substrate structure. Martensite phase includes enormous mismatches in lattices compared with ferrite phase. If the crystalline oxide film forms on the substrate at regular lattice constants, the oxide formed on martensite would contain a large number of defects. The amount of defects in the film is closely related to \( N_D \). The \( N_D \) of 50F50M was close to that of 100M. Chwang and co-workers reported that the value of carrier density of semiconductors depends on grain boundary length or misorientation angle.30 The grain boundary of ferrite and martensite phases probably forms the defective oxide film because its crystal lattice or crystallographic orientation is different from that in each phase. Polarization of iron at a higher potential results in the formation of a thicker passive film on the surface.31 If the specific resistance of the oxide is constant, the resistance of a thick passive film should be larger than that of a thin one. Assuming that the passive film of iron consists of a bi-layer of inner Fe3O4 and outer \( \gamma \)-Fe2O3, most of the electric conductivity would be caused by the Fe3O4 layer rather than by the \( \gamma \)-Fe2O3 layer.11,25 It is known that after oxidation of the iron substrate to \( \gamma \)-Fe2O3, Fe3O4 forms thermodynamically and grows at the interface between the substrate and \( \gamma \)-Fe2O3 layer. The distorted and disordered surface structure of martensite phase is effective for enlarging the reaction activity of Fe3O4 formation. Formation of a bi-layer of thicker Fe3O4 and thinner \( \gamma \)-Fe2O3 formed on martensite results in a smaller resistance than that on ferrite phase.

**SECM.—** The tip generation substrate collection mode SECM using an FcMeOH mediator was carried out in order to investigate the electrochemical reactivity of the 50F50M surface in pH 8.4 boric acid-borate buffer solution. Figs. 8a and 8b show tip current images of the surface after film formation at 0.7 V (SHE) for 3600 s. In the image, the upper right corner of the specimen piece embedded in resin is distinguished with a large difference in tip current. The tip current is due to oxidation of FcMeOH in a narrow space between the microelectrode and substrate. If the product of [FcMeOH]3+ can be reduced to FcMeOH on the substrate, a relatively large current flows through the microelectrode. Thus, the tip current would correspond to electrochemical reactivity of the substrate surface. Since the surface is covered with an oxide film, the reactivity is closely related to the semiconductive property and thickness through the oxide film.33 It was reported that a thinner or defective film results in a larger tip current than that in the case of a thicker or defect-free film.16,17 The distribution of tip current in the image clearly indicated that the oxide film formed on dual-phase steel is non-uniform in electrochemical reactivity. Figs. 8c and 8d are optical microscopic images of the same surface as that in Figs. 8a and 8b, respectively. In the optical image (Fig. 8c), martensite phase has a mottled pattern and can be distinguished from ferrite phase. Dark and gray parts showing smaller currents in the SECM images corresponds to ferrite phase, while white parts showing larger currents are martensite phase. It is thought that martensite phase is covered with an oxide film that has high electric conductivity and with probably a thinner and/or defective oxide film than that on ferrite phase. Moreover, ferrite phase allows a relatively large scattering of tip current as dark and gray parts in the image, indicating that the oxide film has heterogeneity in conductivity. This is probably due to dependence of the film property on crystallographic orientation of the substrate. Since the mean grain size of ferrite phase is several tens of micrometers, which is larger than that of martensite phase, the anisotropic difference in the oxide property could be distinguished in SECM imaging with a microelectrode of 10 \( \mu \text{m} \) diameter.

![Figure 6](image-url)

**Figure 6.** Mott-Schottky plots of carbon steels after film formation at \( E_f \) = 0.9 V (SHE) for 3600 s.

![Figure 8](image-url)

**Figure 8.** (a,b) SECM probe current images and (c-e) optical microscopic images of the dual-phase steel (50F50M) surface passivated at 0.7 V for 3600 s. In SECM measurement, potentials of an SECM microelectrode tip and the steel substrate were held at \( E_f = 0.6 \) V (SHE) and \( E_s = 0.1 \) V (SHE), respectively. A microelectrode with a diameter of 10 \( \mu \text{m} \) was scanned in a 500 \( \mu \text{m} \) square area with an interelectrode distance of 5 \( \mu \text{m} \).
This finding is in agreement with the findings of previous studies\textsuperscript{14,15} in which polycrystalline pure iron was covered with various passive films depending on the crystallographic orientation.

**Passive film formed on dual-phase carbon steel.**—The electrochemical measurements discussed above revealed that the electrochemical properties of the passive film on 100F are superior to those of the passive film on 100M and that the passivity of 50F50M is intermediate between that of 100F and that of 100M. This seems reasonable since 50F50M is composed of ferrite and martensite phases. Furthermore, SECM measurements clearly showed a heterogeneous distribution of electrochemical reactivity of the passivated dual-phase steel surface. Although the effect of grain boundaries should be discussed in detail, SECM showed no evidence about the electrochemical activity on grain boundaries. However, it is expected that the passivity of dual-phase steel diminishes because of the property of martensite phase rather than that of ferrite phase.

Fig. 9 shows a schematic diagram of the structure of a passive film formed on dual-phase carbon steel. Compared with ferrite phase, a large amount of surface iron on martensite phase might be oxidized because of the high reaction activity due to distortion or dislocation of the substrate. However, there are more defects in the passive film formed on martensite phase than in the passive film formed on ferrite phase. Although the film is composed of inner Fe$_3$O$_4$ and outer $\gamma$-Fe$_2$O$_3$ bi-layers,\textsuperscript{30,31} the electrochemical measurements suggest that the Fe$_3$O$_4$ layer is relatively thick and/or the $\gamma$-Fe$_2$O$_3$ layer is relatively defective on martensite phase compared with those on ferrite phase. This results in the difference in electrochemical properties of the films on martensite and ferrite phases and the heterogeneous distribution of film properties on dual-phase steel. In SECM, reduction current on martensite and ferrite phases and the heterogeneous distribution of film properties on dual-phase steel surface. Although the effect of grain boundaries should be discussed in detail, SECM showed no evidence about the electrochemical activity on grain boundaries. However, it is expected that the passivity of dual-phase steel diminishes because of the property of martensite phase rather than that of ferrite phase.

**Conclusions**

Dual-phase carbon steel composed of ferrite and martensite (50F50M) as well as pure ferrite phase steel (100F) and pure martensite phase steel (100M) was polarized in pH 8.4 boric acid-borate buffer solution and the following results were obtained.

1. The corrosion potentials of the steel surfaces after removal of the air-oxidized films are in the order, 100F < 50F50M < 100M, while the corrosion potentials after galvanostatic reduction are in the inverse order, 100M < 50F50M < 100F.

2. Passivity-maintaining current is in the order of 100F < 50F50M < 100M.

3. Charge transfer resistance and film capacitance of the passivated surfaces measured by EIS are in the order of 100F < 50F50M < 100M.

4. 50F50M shows the largest donor density of the films among the three steel substrates, while they have little difference in flatband potential. SECM measurement of 50F50M revealed that electronic conductivity through a passive film on martensite phase was larger than that through a passive film on ferrite phase, even though there is variability in the conductivity on ferrite phase owing to crystallographic orientation and relatively large grain size.

From the above findings, it was concluded that the passive film formed on dual-phase carbon steel has electrochemical properties intermediate between those on ferrite and martensite phases and that the passivity of dual-phase steel is governed by partial passivity of martensite phase.

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Figure 9. Schematic diagram of the structure of a passive film on dual-phase carbon steel.