Formation of Porous Anodic Films on Carbon Steels and Their Application to Corrosion Protection Composite Coatings Formed with Polypyrrole

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The growth behavior of nanoporous anodic films on carbon steel containing 0.213 mass % carbon has been examined. The films were grown by anodizing in an ethylene glycol (EG) electrolyte containing 0.1 mol dm−3 NH4F and 0.5 mol dm−3 H2O. The steel contains carbide precipitates with sizes in the range 50–800 nm. The anodic film formed on the carbide phase grew more slowly and was more chemically soluble during anodizing, resulting in submicrometer pits on the anodic film. The nanoporous morphology of the anodic films formed on an α-Fe matrix resembled those formed on iron. Heat treatment of the anodized specimens caused transformation of the chemically soluble fluoride-containing amorphous or poorly crystalline anodic films to crystalline oxide films containing α-Fe2O3 and Fe3O4. Polypyrrole (PPy) was electropolymerized on the transformed surfaces to form a corrosion-protective composite coating. The resultant specimens coated with the composite coating showed improved durability compared to passivated steel with a PPy coating.

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Porous oxide films formed on aluminum and magnesium alloys by anodizing have been extensively studied for their ability to protect alloys from corrosion and wear; in addition, an anodizing process is of fundamental interest for the growth of self-ordered porous films.1–3 Recently, attention has been drawn to the formation of highly ordered nanoporous structures on aluminum, which are formed by the anodizing process, and their use in nanoscience and nanotechnology.4 Furthermore, the formation of self-ordered nanoporous oxide films on a range of metals, including titanium, zirconium, niobium, tantalum, tungsten is of interest.11,12

Iron is the most widely used metal. Recently, self-ordered nanostructured oxide films have been developed on iron using organic electrolytes containing fluoride and trace amounts of water.15–26 Depending upon the anodizing conditions, either nanoporous or nanotubular anodic films are formed on iron.14,18,24,27 The as-formed anodic films are often amorphous and contain a relatively high concentration of fluoride species; however, such films are not chemically stable. Heat treatment of the anodized iron samples causes crystallization of the amorphous anodic film, forming mainly α-Fe2O3.16,17,21 α-Fe2O3 is a promising material for solar-driven water splitting due to its low bandgap, low cost, abundance, and high chemical stability; consequently, nanostructured porous α-Fe2O3 films formed by anodizing and subsequent heat-treatment have recently attracted much attention.17,18

In addition to photocatalytic applications, porous anodic films on iron can be used to protect iron and steel from corrosion. Iron and steel alloys are often coated with paints to protect them from environmental corrosion. In addition, interest in the use of conducting polymer coatings has increased because they provide anodic protection due to their oxidizing ability; in addition, they act as a physical barrier, protecting the metal.28–31 By using inhibitor anion species as dopants in the conducting polymer, specimens coated with such conducting polymers show improved corrosion protection.32–34 However, conducting polymers adhere poorly to metallic substrates.35

In the present study, an attempt has been made to prepare composite coatings, consisting of a porous anodic film and electropolymorized polypyrrole, on carbon steel that show improved corrosion protection and adhesion. Because the formation behavior of the anodic films on carbon steels is still unclear, the growth, before the deposition of polypyrrole, of the anodic films on carbon steel containing 0.213 mass % carbon has been examined in detail.

Experimental

A carbon steel plate with a composition of Fe: 99.204 mass %, C: 0.213 mass %, Si: 0.016 mass %, Mn: 0.550 mass %, P: 0.014 mass %, and S: 0.003 mass % was used in this study. For comparison, an iron (99.99 mass %) plate was also used. In addition, magnetron-sputtered Fe-30 at.% C films were also prepared on a glass substrate using a Shimadzu SP-2C system. The target consisted of a 99.99% pure iron disc of 100 mm in diameter, on the erosion region of which four graphite discs of 24 mm diameter were placed symmetrically. After evacuating the chamber to less than 6 × 10−5 Pa, deposition of the alloy films was conducted at 0.5 A in an argon atmosphere of ~0.3 Pa for 10 min. To obtain a uniform composition and thickness of the deposited film, the substrate holders were rotated around the central axis of the chamber as well as their own axes during deposition. The composition of the deposited film, examined by a JEOL JXA-8530F field-emission electron probe microanalyzer, was Fe-30 at.% C, and the film was identified to be amorphous from XRD measurements.

Prior to anodizing, the bulk plate specimens were mirror-polished using an alumina abrasive of 1 μm diameter; then, radiofrequency glow discharge (RF-GD) sputtering was carried out using a Jobin-Yvon 5000 RF instrument in an argon atmosphere of 700 Pa by applying an RF of 13.56 MHz and a power of 40 W for 5 s to obtain clean and relatively flat surfaces. The magnetron-sputtered Fe-30 at.% C films were used without pretreatment before anodizing. Anodizing was carried out galvanostatically at a constant current density of 50 A m−2 for several periods of time in ethylene glycol electrolyte containing 0.1 mol dm−3 NH4F and 0.5 mol dm−3 H2O at 293 K. The PPy layer was formed on the anodized specimens after heat treatment; in addition, a PPy layer was formed on a passivated carbon steel specimen. The heat-treatment was conducted in argon at 673 K for 30 min. The passivation treatment was performed at 0.8 V vs. Ag/AgCl in an aqueous Na2MoO4 solution (0.06 mol dm−3) for 15 min. For the electropolymorization of PPy, a three-electrode cell with an Ag/AgCl reference electrode and a platinum foil counter electrode was used. The electrolyte was an aqueous H3PO4 solution (a 0.2 mol dm−3) containing 0.1 mol dm−3 pyrrole monomer and
5 mmol dm$^{-3}$ H$_3$PMO$_{12}$O$_{40}$. The solution was prepared in deionized Milli-Q water, which was deoxygenated by nitrogen bubbling for 30 min prior to use. The electropolymization was performed at a constant current density of 10 A m$^{-2}$ for 30 min at room temperature to deposit an approximately 5-μm-thick PPy layer. Adhesion tests of the coated specimens were performed according to ASTM D 3359–97. The corrosion of the coated specimens was examined by immersing the specimens in 3.5% NaCl solution at room temperature, and the corrosion potential was monitored during immersion.

The surface distribution of elements of the carbon steel was analyzed using a JEOL JAMP-9500F field emission Auger microprobe (Auger electron spectroscopy, AES), operated at an accelerated voltage of 25 kV. A flat surface for AES analysis was obtained by a JEOL SM-09010 cross-section polisher. The surface and fracture sections of the anodized specimens were observed using a JEOL JSM-6500F field emission scanning electron microscope, operated at an accelerating voltage of 10 kV. The cross-section of the anodized specimens was also examined by a JEOL JEM-2000Fx transmission electron microscope operated at 200 kV. Electron transparent sections were prepared using a Hitachi, FB-2100 focused ion beam system.

Elemental depth profile analysis of the PPy-coated specimens was performed using a Jobin-Yvon 5000 RF-GD optical emission spectroscopy (GDOES) instrument in a neon atmosphere at 1100 Pa by applying an RF of 13.56 MHz with a power of 50 W. Neon gas was used to excite emissions from fluorine because no excitation was observed with conventional argon gas. Light emissions of characteristic wavelengths were monitored throughout the analysis with a sampling time of 0.1 s to obtain depth profiles. The wavelengths of spectral lines used were 121.567 nm for hydrogen, 165.701 nm for carbon, 130.217 nm for oxygen, 685.602 nm for fluorine, 178.287 nm for phosphorus, 385.991 nm for iron, and 317.035 nm for molybdenum. Signals were detected from a circular area of approximately 4 mm diameter.

Results and Discussion

Formation of anodic films on carbon steel.—Figure 1 shows a scanning electron micrograph of the carbon steel and the corresponding AES element images for iron, carbon, and manganese. The scanning electron micrograph (Fig. 1a) shows that the carbon steel grains are several micrometers in size. In addition, the presence of many precipitated particles with sizes ranging from 50 to 800 nm is evident in this micrograph. The EDS element images show that the precipitates must be iron carbide (Fe$_3$C). The carbon steel contains 0.55 mass% manganese with the content being higher than that of carbon; however, no detectable precipitation and segregation of manganese can be seen in Fig. 1d, suggesting that manganese is dissolved homogeneously throughout the α-Fe matrix phase.

Figure 2 shows the voltage-time curves of the iron and carbon steel during anodizing at a constant current density of 50 A m$^{-2}$. Both specimens showed an initial voltage surge of around 6 V at the commencement of anodizing, mainly due to the resistivity of the electrolyte. Then, the iron specimen showed an approximately linear voltage rise to ∼10 V at a rate of 0.04 V s$^{-1}$, followed by a steep voltage rise. Then, a quasi-steady voltage of 33–34 V was reached. The voltage-time curve of the carbon steel is similar to that of the iron sample, and both specimens showed similar anodizing voltages after anodizing for 30 min.

The surfaces of the iron and carbon steel before and after anodizing were observed by SEM. Figure 3 shows the surface images of the anodic films on iron. After anodizing for 20 s (Fig. 3a), at which the formation voltage reached 7 V, only step-like features, originating from the RF-GD sputtering of the substrate, are seen; no nanopores were found in this micrograph. Thus, a barrier–type anodic film was formed after 20 s. On anodizing for 100 s, the formation voltage rose to 10 V and the nanoporous anodic film formed, as is clearly shown in Fig. 3b. Interestingly, nanopores developed preferentially along with steps and at “kink-like” sites. In anodizing of aluminum, nanoscale recessions at the substrate surface were preferential sites for the formation of nanopores. Thus, the prepatternning of the aluminum surface by nanoimprinting and electron-beam lithography has been used for fabrication of ideally ordered nanoporous anodic alumina films. Our findings suggest that preferential pore initiation also occurs in nanoporous anodic films on iron-based materials. On further anodizing for 300 and 1800 s (Figs. 3c and 3d), the step-like features on the film surface became unclear, probably due to chemical dissolution of the anodic films on the film surface.

Figure 4 shows the surfaces of anodic films formed on the carbon steel at different anodizing times. Local recessions formed after anodizing for 20 s (Fig. 4a), being more obvious after anodizing for 100 s (Fig. 4b). In the recessions on the surface, no nanopores were visible, while nanoporous oxides were generated in the surrounding area after anodizing for 100 s. The sizes of the recessed areas are similar to those of the iron carbide grains, as shown in Fig. 1, suggesting that the recessions formed on the iron carbide phase. Furthermore,
nanopores developed on the carbide phase after anodizing for 200 s (Fig. 4c). The pore size on the carbide phase is larger than that on the surrounding \( \alpha \)-Fe phase. In particular, larger pores are often present at high densities at the boundaries between the two phases (\( \alpha \)-Fe and carbide). The surface morphology after anodizing for 300 s (Fig. 4d) is similar to that after 200 s, but anodic oxide on the carbide phase appears to have dissolved almost completely, forming pits in the anodic film after anodizing for 30 min (Fig. 4e). The difference of the surface morphology of the anodic films formed on the iron and carbon steel for 30 min is shown clearly in Fig. 5; submicrometer pits developed only on the carbon steel sample, and their distribution is similar to that of the distribution of carbide (Figs. 1a and 1c).

Growth of anodic films on magnetron-sputtered Fe-30 at.% C alloy.—To better understanding the anodic film growth on iron carbide (Fe\(_3\)C), a magnetron-sputtered solid-solution Fe-30 at.% C film with an amorphous structure was prepared. Figure 6 shows the voltage-time and current-time curves of iron and the Fe-30 at.% C alloy during anodizing at a constant current density of 50 A m\(^{-2}\) and a constant voltage of 35 V, respectively. Anodizing of the Fe-30 at.% C alloy at a constant current density resulted in a continuous increase in the anodizing voltage to more than 150 V, while that of iron shows a steady voltage of \( \sim \) 35 V (Fig. 6a). When the Fe-30 at.% C and iron samples were anodized at 35 V, both specimens showed a steady current density after an initial rapid current decrease. The steady current density of...
the Fe-30 at.% C specimen was lower than that of the iron specimen. During anodizing of the carbon steel at a constant current density, a steady anodizing voltage of \( \sim 35 \text{ V} \) was observed (Fig. 2). The results shown in Fig. 6 suggest that the growth of the anodic film on the iron carbide phase is slower than that on the \( \alpha \)-Fe phase at 35 V because of the lower current density of the Fe-30 at.% C specimen compared with that of the iron specimen. In fact, scanning electron micrographs of cross-sections of the iron and Fe-30 at.% C specimens after anodizing at 35 V for 200 s (Fig. 7) show that the anodic film on the latter substrate was thinner than that of the former. The relationship between film thickness and anodizing time (Fig. 8a) is approximately linear. The anodic film on the Fe-30 at.% C specimen is thinner than that of the iron specimen at any anodizing time. Figure 8b shows the change in film thickness with the electric charge passed though the sample during anodizing. Interestingly, thicker anodic films are formed on the Fe-30 at.% C specimen compared to those on iron at the same electric charge. On both substrates, the film thickness increases linearly with the electric charge.

After anodizing the Fe-30 at.% C at 50 A m\(^{-2}\) to selected voltages, the thickness of the barrier layer between the porous layer and alloy substrate was measured from scanning electron micrographs of fractured cross-sections. The thickness of the barrier layer increases linearly with the anodizing voltage (Fig. 9a), which is characteristic behavior of anodic films on metals.\(^{39}\) The thickness increases at a rate of \( 1.6 \pm 0.1 \text{ nm V}^{-1} \), and this value is lower than that on iron. The reduced value indicated that a higher electric field was applied in the barrier layer on the Fe-30 at.% C in comparison with that on iron, probably because of the incorporation of carbon species derived from the substrate. Transmission electron micrographs of the Fe-30 at.% C specimen anodized at 50 A m\(^{-2}\) for 200 s show fine gas bubbles (light spots, indicated by arrows) in the barrier layer beneath the porous layer (Fig. 9b). EDS analysis of the barrier layer indicates that carbon...
Figure 8. Change in the thickness of the anodic films formed on magnetron-sputtered Fe-30 at.% C and iron with (a) anodizing time and (b) electric charge. Anodizing was performed at a constant voltage of 35 V in ethylene glycol electrolyte containing 0.1 mol dm$^{-3}$ NH$_4$F and 0.5 mol dm$^{-3}$ H$_2$O.

is not present, and this may be due to the formation of gas (CO or CO$_2$) during anodizing of the Fe-30 at.% C specimen, the gas then becoming incorporated in the barrier layer as gas bubbles and, subsequently, being released during preparation of the thin electron-transparent sections. The presence of gas bubbles enhances the electric field strength in the growing barrier layer during anodizing, reducing the thickness of the barrier layer.

Our findings suggest that growth of anodic films on the iron carbide phase is slower than that on the $\alpha$-Fe phase. On the iron carbide phase, recessed areas develop on the submicrometer carbide phase, which are dispersed through the $\alpha$-Fe matrix phase of the carbon steel. In addition, we found that faster chemical dissolution of the anodic films on the carbide phase occurred in comparison with that on $\alpha$-Fe phase during immersion of the anodized carbon steel in the electrolyte. In addition, GDOES elemental depth profiles of the anodized iron and Fe-30 at.% C specimens showed increased concentration of fluorine and carbon species in the anodic film on the latter substrate compared with that on the former. During the anodizing of titanium in fluoride-containing electrolytes, fluoride species become enriched at cell boundaries of the porous anodic films, and, as a consequence of preferential chemical dissolution of the fluoride-rich cell boundaries, anodic films with nanotubular morphology formed.\textsuperscript{40,41} The increased concentration of fluoride and carbon species may enhance the chemical dissolution of anodic films, contributing to the development of submicrometer pits in the anodic films observed on the carbon steel. The process of formation of pits on the anodic film pits on carbon steel is illustrated in Fig. 10.

In the initial anodizing of the carbon steel at which a porous layer is initiated on $\alpha$-Fe phase, only a thin barrier layer is developed on the carbide phase (Step 1 in Fig. 10). Because of higher ionic resistivity of the barrier layer formed on the carbide phase, the subsequent growth of the porous layer is also slower on the carbide phase rather than that on the $\alpha$-Fe phase (Step 2 in Fig. 10). In addition, the chemical dissolution of the anodic film formed on the carbide phase is faster than that on the $\alpha$-Fe phase (Step 3 in Fig. 10). Both the slower growth of the porous layer and faster chemical dissolution of the porous layer on the carbide phase contribute to the formation of submicrometer pits associated with the presence of the carbide phase in the carbon steel (Steps 4 and 5 in Fig. 10).

Corrosion-resistant PPy/anodic oxide composite coating.—After the formation of an anodic film containing a number of submicrometer pits on the carbon steel, heat-treatment was conducted to transform the amorphous fluoride-containing anodic film to a fluoride-free oxide film containing Fe$_3$O$_4$ and $\alpha$-Fe$_2$O$_3$ phases. The presence of these two crystalline phases was confirmed by XRD measurements, and the results are consistent with those formed on iron.\textsuperscript{42} SEM observations

Figure 9. (a) The change in thickness of the barrier layer of the anodic films formed on the magnetron-sputtered Fe-30 at.% C film as well as high purity iron with anodizing voltage and (b) transmission electron micrograph of FIB cross-section of the magnetron-sputtered Fe-30 at.% C film anodized at a constant current density of 50 A m$^{-2}$ in ethylene glycol electrolyte containing 0.1 mol dm$^{-3}$ NH$_4$F and 0.5 mol dm$^{-3}$ H$_2$O for 200 s.
revealed no obvious morphological changes on the heat-treatment, which is similar to SEM results on anodized films formed on iron.

The deposition of a PPy layer was performed on the anodized carbon steel after heat-treatment and also on passivated carbon steel. Deposition was carried out by electropolymerization of pyrrole monomer in the presence of H₃PMo₁₂O₄₀, which was incorporated into the PPy layer as a dopant and also inhibitor. The electropolymerization proceeds at \( \sim 0.6 \) V vs. Ag/AgCl for both specimens (Fig. 11), being similar to those previously reported for iron. The pits in the anodic film formed on carbon steel (Fig. 5b) were completely filled with PPy. After dissolving the substrate and anodic film in HCl solution, the remaining PPy was observed by TEM (Fig. 12c). PPy nanofibers with a fiber diameter of 20–30 nm are seen in this micrograph. Most nanofibers appear to be solid, but hollow nanofibers are locally present as indicated by an arrow. The formation of hollow nanofibers is associated with the deposition of PPy on almost all of the walls of iron oxide nanopores, not on the bottom of the pores. The pore walls consisted mainly of conductive Fe₃O₄ such that the deposition of PPy occurred on the pore walls.

Adhesion tests according to ASTM D 3359–97 revealed that no detachment of the PPy layer occurred for the cross-scratched PPy/anodic oxide composite coatings in contrast to the partial detachment of the PPy layer formed on the passivated carbon steel. The improved adhesion must be associated with the deposition of PPy even in the

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**Figure 10.** Schematic illustrating showing a growth process of the anodic film with pits on the carbide phase during anodizing of the carbon steel.

**Figure 11.** Potential transient during electropolymerization of pyrrole on the carbon steel with anodic and passive films at a constant current density of 10 A m⁻² in 0.2 mol dm⁻³ H₃PO₄ solution containing 0.1 mol dm⁻³ pyrrole monomer and 5 mmol dm⁻³ H₃PMo₁₂O₄₀.

**Figure 12.** (a,b) Scanning electron micrographs of surface of PPy layer deposited on the carbon steel with (a) anodic and (b) passive films at a constant current density of 10 A m⁻² in an aqueous 0.2 mol dm⁻³ H₃PO₄ solution containing 0.1 mol dm⁻³ pyrrole monomer and 5 mmol dm⁻³ H₃PMo₁₂O₄₀ and (c) transmission electron micrograph of PPy nanofibers deposited in the porous anodic film.
Figure 13. GDOES elemental depth profile of carbon steel with a PPy/anodic oxide composite coating.

Figure 14. Change in the corrosion potential of carbon steel with and without PPy/anodic oxide or PPy/passive oxide coatings during immersion in 3.5% NaCl solution. For comparison, the result of the iron with a PPy/anodic oxide composite coating is also shown.

Conclusions

1. Anodic films formed on a carbon steel with submicrometer iron carbide precipitates contain a number of submicrometer pits in the anodic films in addition to nanometer pores. The pits develop on the iron carbide phase.
2. The growth of the anodic films on iron carbide is slower than that on α-Fe and also the chemical dissolution rate of the anodic film on iron carbide is faster than that on α-Fe. As a consequence, pits develop in regions containing the iron carbide phase at the surface.
3. A PPy layer is formed on the anodized carbon steel after heat-treatment, and the PPy penetrates the nanopores. The submicrometer pits are also filled with PPy.
4. In a 3.5% NaCl solution, the carbon steel with the PPy/anodic oxide composite coating shows highly improved corrosion resistance in comparison with that of the PPy/passive oxide coating.

The corrosion protection of the coated specimens was examined by monitoring the corrosion potential in 3.5% NaCl solution. Figure 14 shows the change in corrosion potential with immersion time for the carbon steel with the PPy/anodic oxide composite coating and PPy/passive film coating. The results of the non-coated carbon steel and the iron with the composite coating are also shown for comparison. The corrosion potential of the non-coated carbon steel stabilized at a negative potential of −0.66 V vs. Ag/AgCl in the early stages of immersion where corrosion proceeded. In contrast, the corrosion potential of the coated specimens remained at a positive potential (0.1–0.2 V vs. Ag/AgCl). These specimens are in the passive state and well protected from corrosion in the chloride solution. The corrosion potential shifted drastically to a negative potential at less than 30 ks for the carbon steel with a PPy/passive film coating, while the passive potential was observed until 150 ks for the specimens with the PPy/anodic oxide composite coating on both carbon steel and iron. The highly improved durability of the PPy/anodic oxide composite coating compared with that on the PPy/passive film coating on carbon steel is in agreement with the previous study on iron. Furthermore, the similar durability of the composite coatings on carbon steel and iron shown in Fig. 14 indicates that the presence of a number of submicrometer pits in the anodic film on carbon steel has no negative influence on the corrosion protection.

The ennobled corrosion potential in the passive state due to the presence of the PPy coating is caused by the ability of oxidized PPy to act as an oxidizer (anodic protection). During immersion in a corrosive environment, reduction of the oxidized PPy, which is electrically conductive, proceeds, along with oxidation of the substrate. The reduction of PPy releases dopant anions to maintain the charge balance in the conducting polymer. If inhibitor anions are used as dopant anions, their release also suppresses the active dissolution of the substrate at the defect sites in the conducting polymer coating. To examine the release behavior of dopant anions from the PPy/anodic oxide composite coating during immersion in the NaCl solution, GDOES elemental depth profile analyses were performed. Figure 15 shows the depth profiles obtained before and after immersion of the PPy/anodic oxide coating on iron. The amount of both molybdenum and phosphorus in the outer part of the PPy coating decreased with immersion time, but their concentrations remained unchanged in the inner part of the PPy coating. The results suggest low mobility of phosphomolybdate anions in the PPy coating. Another interesting feature in the depth profiles is the incorporation of sodium ions in the PPy coating. It is evident that sodium ions were incorporated in the inner part of the coating, with their concentration increasing with immersion time. Although the profiles are qualitative, the incorporation of sodium ions appears to be more significant than the release of phosphomolybdate anions. The incorporation of sodium ions in the inner part of the coating might cause the reduction of PPy in this part. Reduced PPy is less conductive; therefore, it may become difficult to maintain a passive state by anodic protection. Thus, the incorporation of cations in the inner part of the PPy coating is a probable reason for the degradation of the present composite coatings at ~150 ks, as shown in Fig. 14. The predominant incorporation of cations in PPy containing relatively large anion dopants during reduction has also been reported previously, and the size of the dopant anions is one of the critical factors controlling the degradation modes; that is, by either dopant release or cation incorporation of the conducting polymer coatings on metals and alloys.
Figure 15. GDOES elemental depth profiles of carbon steel with a PPy/anodic oxide composite coating (a) before and after immersion in 3.5% NaCl solution for (b) 24 and (c) 58 h.

Acknowledgments

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