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Corrosion Resistance of Stainless Steels Analyzed by Fractal Geometry

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ABSTRACT

Fractal property of the passivated steel surface was investigated on the basis of scaling analysis with a special focus on its relationship with corrosion resistance. For this purpose, the surface of stainless steel was intentionally oxidized under a variety of passivation conditions and its scaling property was analyzed by a triangulation method. The morphology of the passivated steel surface was satisfactorily evaluated with fractal dimension. From the chronoamperometry and impedance measurement, it proved that lower fractal dimension leads to more enhanced corrosion resistance. The higher passivity of the steel surface with lower fractal dimension was discussed in terms of active area and structural imperfection.

Keywords : Fractal dimension, Scaling property, Stainless steel, Surface roughness

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1. Introduction

Morphology is regarded as one of the most important surface properties because it is implicit in essential reaction factors including surface activity and structural defects. For the quantitative analysis of surface morphology, the rms roughness has been usually used. Although the rms roughness reflects well the information on the simple vertical fluctuation of the surface, however, it fails to include more details on the actual three dimensional (3D) surface roughness. Thus, it has not been so useful for the researchers who try to explain their experimental data based on the structure of materials surface.

In contrast, the fractal approach to surface enables one to collect the in-depth information of 3D surface irregularity, with the help of a scaling analysis using yardsticks with different sizes.[1-6] That is, fractal dimensions involving the degree of 3D surface roughness can be evaluated over a wide spatial cut-off range. In this regard, the usefulness and accuracy of a triangulation method to quantify a self-similar fractal dimension has been suggested[7] and the method has been recently applied to investigate the surface properties of passivated surface of stainless steels.[8]

In this communication, we present our preliminary results on the qualitative relationship between corrosion resistance and fractal dimension of stainless steel. Especially, the steel surfaces were deliberately oxidized to have different surface irregularities and their fractal dimensions were calculated at different scales. The steady-state current level and impedances were measured for each sample and the results were discussed in terms of the active surface area and structural imperfection of passive film.dk

2. Experimental Details

For the morphological and electrochemical characterization, standard 304 stainless steels were intentionally oxidized to form three kinds of surface oxide films with different irregularity: (1) the sample was first electro-polished at 30°C in a 2 : 1 : 1 volume mixture of

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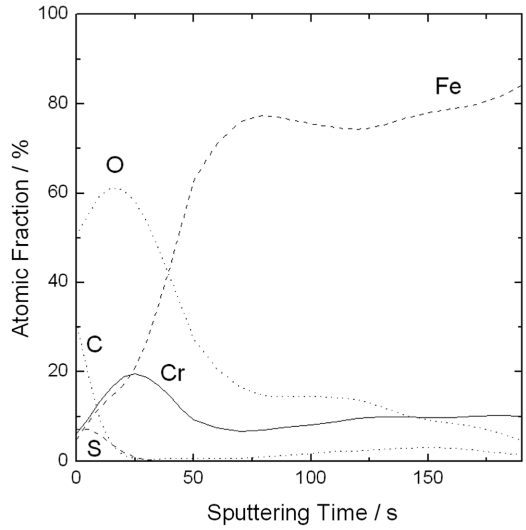
H_3PO_4, H_2SO_4 and glycerol, followed by the application of cathodic current of 0.5 Acm^{-2} for 300 s in an aqueous solution of 5 M H_2SO_4,[9] (2) the sample was polished with 240, 600, 1200 SiC paper in sequence and finished with a 1 μm diamond suspension for mirror-like surface. Then, a constant potential of –0.1 V *vs.* SCE (active-passive transition region) was applied for 1200 s in an aqueous solution of 5 M H_2SO_4, (3) after the pretreatment of the sample in the same manner as the method (2), constant potentials of 0.17 (passive region) and 1.29 V *vs.* SCE (trans-passive region) were alternately applied for 0.04 s each in an aqueous solution of 5 M H_2SO_4. This process was repeated for 1200 s.[10] Based on the smoothness of bare substrate and stability of oxides in the course of overall oxidation process, (1), (2) and (3) possibly produce "compact film", "porous film", and "highly-porous film", respectively. Incidentally, compact and porous films were also created on ferritic 445NF stainless steels in the same manner as 304 stainless steels in order to make sure the usefulness of the proposed method for other type of steel.

Samples with compact, porous, and highly-porous films were vacuum-sealed immediately after drying under nitrogen gas flow to minimize the surface oxidation in the air. The fractional content of atomic elements in each film was analyzed using Auger electron spectroscopy (AES, PHI-700, ULVAC-PHI). The surface morphology was imaged using atomic force microscope (AFM, XE-120, Park Systems) by scanning over an area of $1 \times 1\ \mu m^2$ with a resolution of 256×256 pixels, and (x, y, z) coordinate of each pixel was collected. Then, the fractal dimension of the sample surface was estimated by a triangulation method.[7]

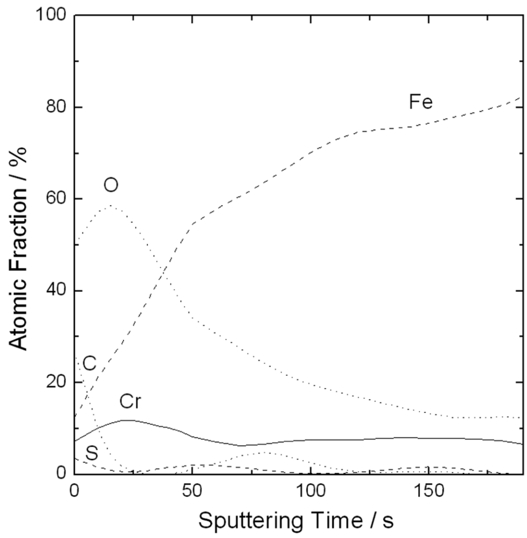
Steady-state current of each sample was recorded in an aqueous solution of 5 M H_2SO_4 by applying its open circuit voltage obtained right after the formation of oxide film. Impedance spectra were subsequently obtained at open circuit voltage in the same solution over the frequency range of 100 kHz to 1 Hz. A platinum mesh and a saturated calomel electrode (SCE) were adopted as the counter and reference electrodes, respectively. All the electrochemical measurements were performed with a flat cell (EG&G Model K0235) using IviumStat (IVIUM Technologies, Netherlands).

3. Results and Discussion

Shown in Fig. 1 are the AES depth profiles of the 304 stainless steels with compact and porous oxide film. After the surfaces were etched away for about 50 s, the Cr contents became constant and close to the composition in the bulk and O contents dropped to half of the maximum value, indicating that the interface between oxide and metal was exposed by that time. From the calibration of sputtering rate using Ta_2O_5, the thickness of the compact oxide film was estimated to be about 5 nm. It is noted that the atomic



(a)



(b)

Fig. 1. AES depth profiles obtained from the 304 stainless steels with (a) compact and (b) highly-porous oxide film.

fraction of Cr in porous film was near the half the Cr content in compact film. It has been known that the higher proportion of chromium oxide in passive film leads to more tightly-packed dense oxide layer with enhanced corrosion resistance while the iron oxide in it results in loosely-bonded porous layer that is relatively not protective.

Fig. 2 exhibits the AFM images of the 304 stainless steels. The surface irregularity of three samples was quite different to each other, revealing the morphological feature of compact, porous, and highly-porous film as expected in the experimental section. The scaling properties of three samples were analyzed on the grounds of a triangulation method as follows: the projected plane (x, y) on AFM image with an area of l^2 is divided into $2n^2$ equal triangles, and the real plane or surface (x, y, z) is covered by $2n^2$ triangles with a projected size of L ($= l/n$). The scaled surface area of the real surface A is approximated by summating the areas of all triangles. Then, the fractal dimension D_f of the surface is given by $2 - d\ln A/d\ln L$ from the fractal theory.[7)]

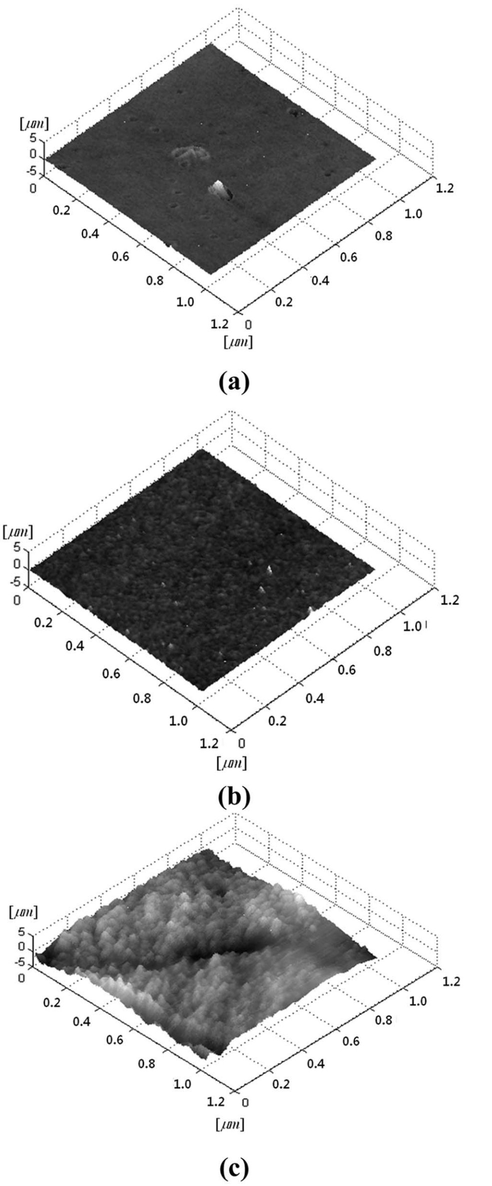


Fig. 2. AFM images obtained from the 304 stainless steels with (a) compact, (b) porous, and (c) highly-porous oxide film.

Shown in Fig. 3 are the scaled surface area A *vs.* projected triangle size L plots for the samples with compact, porous, and highly-porous film. There were roughly two spatial regions having different scaling properties. More specifically, the irregular nature of the surface is abruptly changed at a triangle (or yardstick) size of 100 nm. In particular, the scaling property in the region below 100 nm is worthwhile to note, because it includes the information of the meso-porous surface irregularity around which the active species is dominated by Knudsen transport and it senses the surface in a quite different way from when it does an ideally smooth surface.[11,12)] Accordingly, the difference in the meso-porous irregularity of the oxide film most likely implies that there is dissimilarity in the oxide structure at the micro- to nano-size

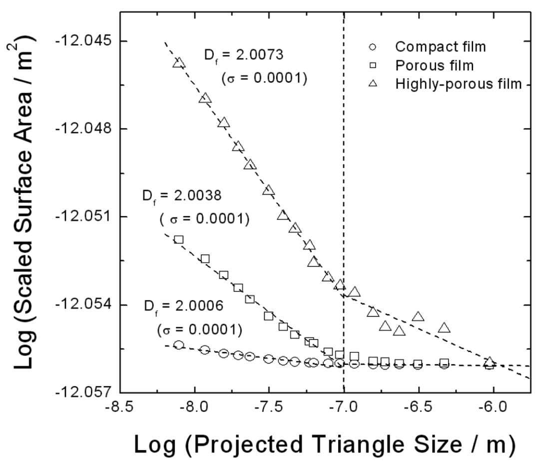
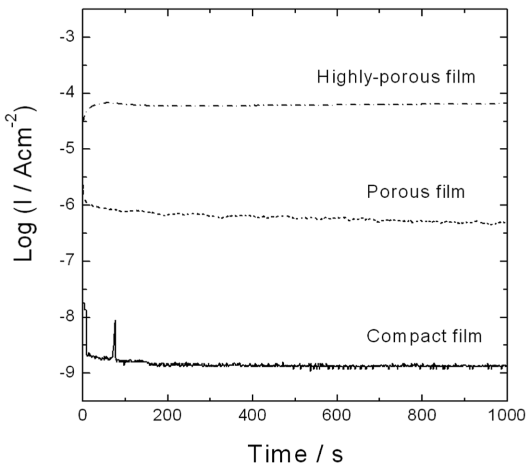


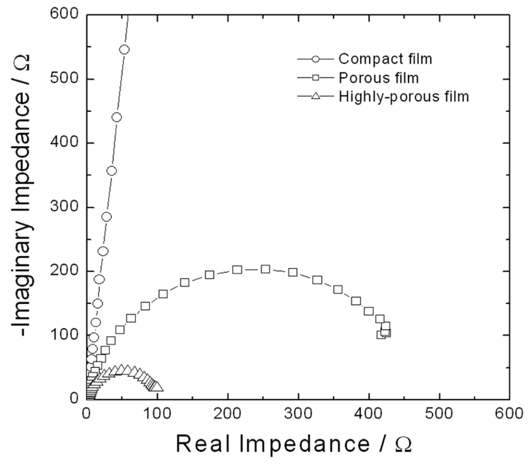
Fig. 3. Variation of scaled surface area with projected triangle size, obtained from the 304 stainless steels with compact, porous, and highly-porous oxide film.

level, *i.e.*, in the structural defect of oxide film. Based on the above explanation, there is great possibility that the higher fractal dimension, *i.e.*, the severer irregularity in the meso-porous regime has a worse effect on corrosion resistance. The fractal dimensions in this spatial region were estimated to be 2.0006, 2.0038, and 2.0073 for compact, porous, and highly porous surface, respectively. Morphological difference was satisfactorily quantified using a fractal dimension with a tolerable standard deviation.

Steady state currents and impedances of three samples were measured for the evaluation of their corrosion resistance. In the chronoamperometric curve (Fig. 4(a)),



(a)



(b)

Fig. 4. (a) Chronoamperometric curves obtained by maintaining the formation potential of oxide films and (b) the corresponding electrochemical impedance spectra.

the current was nearly invariable with time for all three samples, indicative of an excellent stability of the oxide film in the solution. In particular, the steady state current was the highest in the sample with highly-porous surface film, followed by porous film and compact film. Polarization resistance determined from impedance spectra (Fig. 4(b)) showed similar tendency to the steady state current: following the sample with compact film were the samples with porous film and highly-porous film. This means that the porous and highly-porous films are not so effective in protecting the sample against the corrosive environment, as compared to compact layer. This is consistent with the results of scaling analysis of the surface morphologies. In other words, the sample with lower fractal dimension in the spatial region where Knudsen transport dominates showed higher corrosion resistance.

In order to make sure the proposed method is applicable to other type of steel, the surface morphology of passivated ferritic 445NF stainless steel was analyzed in the same manner as above. As a result, there was a clear difference in the fractal dimension between the compact and porous films (Fig. 5(a)). Furthermore, it proved, from steady state currents and impedances (Fig. 5(b)), that the corrosion resistance of the sample with compact layer exceeded that of the sample with porous film, similar to the case of 304 stainless steels.

The reasons for the qualitative relationship between surface irregularity (*i.e.*, fractal dimension) and corrosion resistance might be explained in the following ways: (1) In case that the surface irregularity originates from the porosity of oxide film, large amounts of structural defects such as micro-void, grain boundary, and vacancy can be included in the oxide film with high fractal dimension, as suggested in the compositional analysis of Fig. 1, (2) In case that the surface irregularity comes from the roughness of bare surface beneath the oxide film, the electrochemical active area increases with fractal dimension, which raises the metal dissolution rate. In any case, the quantitative estimation of surface irregularity by fractal dimension might give useful information on the corrosion resistance of stainless steels.

4. Conclusions

In this work, fractal property of the passivated steel surface was satisfactorily analyzed with a special focus

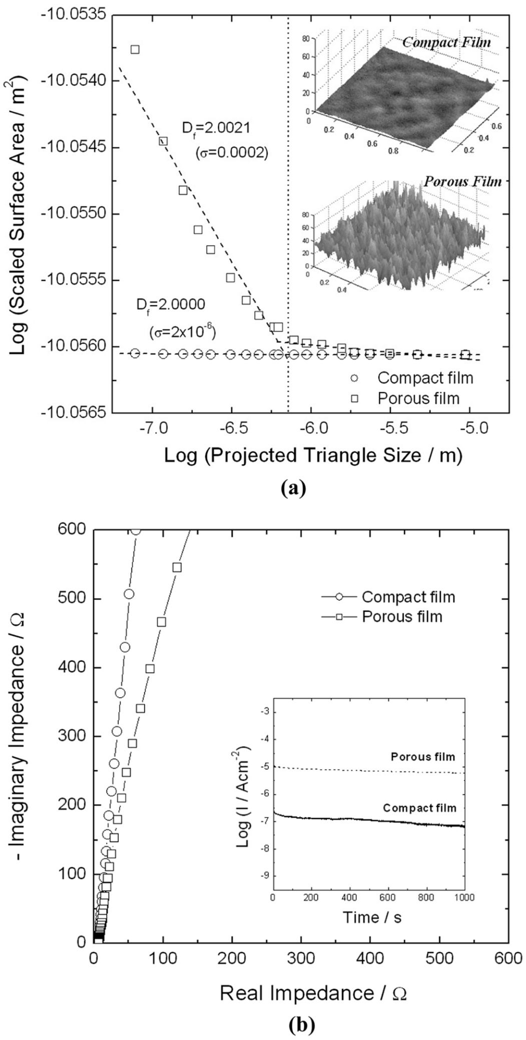


Fig. 5. (a) Variation of scaled surface area with projected triangle size, obtained from the 445NF stainless steels with compact and porous oxide film. The insets are the AFM images of both samples. (b) The corresponding impedance spectra and chronoamperometric curves (inset).

on its relationship with corrosion resistance. The morphology of the passivated steel surface was quantitatively estimated with fractal dimension and it proved, from the steady-state current and impedance spectra, that lower fractal dimension results in more enhanced corrosion resistance. The lower passivity of the steel surface with higher fractal dimension was possibly attributed to large amounts of structural defects included in the oxide film and/or the large electrochemical active area that raises the metal dissolution rate. The quantitative estimation of surface irregularity by fractal dimension might be effectively used to evaluate the corrosion resistance of stainless steels.

Acknowledgements

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