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Characterization of Corrosion-resistant, Nanometer-thick, Layer-by-layer Aluminosilicate Coatings Prepared on Stainless Steel

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ABSTRACT

Highly corrosion-resistant, ~65-nm-thick, layer-by-layer aluminosilicate coatings have been prepared by multiple spin casting on Type 430 stainless steel. These coatings have been characterized by field emission scanning electron microscopy, transmission electron microscopy, conductive atomic force microscopy, and micro-electrochemical measurements using a microcapillary cell. The coatings annealed at 400 °C are non-uniform and contain fine iron oxide nodules, which are formed in high densities on the {111} grain surface of the steel. The iron oxide nodules arise from the outward diffusion of the oxidized iron from the substrate through the coating. The coatings annealed at 400 °C are more insulating compared with those before annealing; however, the nodule sites are less insulating owing to the development of more conductive iron oxide channels in the coatings. A microcapillary cell study reveals that the coated specimens prepared from diluted precursor solutions by a layer-by-layer process exhibit higher pitting potential in 3.5 wt% NaCl solution compared with those prepared through a single-layer process. Moreover, the coated specimen obtained from the layer-by-layer process exhibits similarly high pitting potential even at the flaw sites in the coating; in contrast, the pitting potential in the flaw-containing regions of the coated specimen obtained from a single-layer process shifts towards the less noble direction. The layer-by-layer coating is also effective in suppressing the corrosion of the scratched region of the coated specimens, owing possibly to the excellent adhesion between the coating and the substrate.

1. Introduction

A range of coating systems, including inorganic coatings and paints, have been extensively investigated and widely used as protection against corrosion of metals and alloys. Chromate conversion coatings, which exhibit improved adhesion to paints and self-healing ability [1], are some of the most effective and widely used corrosion-resistant coatings. However, the use of chromates has been restricted owing to their harmful impact on human health and the environment. As a result, several investigations of novel coatings with low environmental impact have been conducted in the last two decades.

Sol-gel coatings can be produced via non-toxic and environmentally friendly processes and hence constitute viable alternatives to the chromates [2,3]. Compared with that of conventional ceramic coatings, the low-temperature processing used in the sol-gel method is especially advantageous for aluminum and magnesium-alloy substrates that degrade at high temperatures. Many oxide coatings based on SiO_2 [4–7], Al_2O_3 [8,9], and ZrO_2 [10,11] have been prepared as protection against the corrosion of steels, stainless steels, Al alloys, and Mg alloys. However, the protection offered by inorganic sol-gel coatings is often inadequate, owing to the cracking of thick coatings [2] and the relatively high porosity of the coatings stemming from the low-temperature processing [6]. Thin 50–120-nm-thick, crack-free SiO_2 coatings were deposited on Type 304 stainless steel using tetraethyl orthosilicate (TEOS) as a chemical precursor. The corrosion current density of the stainless steel in 0.5 mol dm^{-3} H_2SO_4 decreased two orders of magnitude with the coating; however, the pitting potential in 3.5% NaCl solution was still <300 mV vs. SCE [7]. Therefore, increased

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emphasis has been placed on developing organic-inorganic hybrid sol-gel systems for enhancing the barrier nature of the coating. Ooji et al. [12,13] pioneered hybrid coatings and recent progress of hybrid sol-gel coatings used as protection against the corrosion of metallic materials have been reviewed [14].

Although the hybrid sol-gel coatings have significant potential to improve the corrosion resistance of various metals and alloys in corrosive environments, the presence of organic components prevents their use at elevated temperatures (>300 °C). A layer-by-layer sol-gel processing method has recently been introduced as a means of producing highly dense and defect-free thin oxide films that consist only of inorganic species. The oxide films formed by this processing exhibit excellent dielectric [15,16] and proton-conducting [17–23] properties. Recently, some of the present authors applied this layer-by-layer processing to the fabrication of dense nanometer-thick aluminosilicate coatings to be used for the protection of stainless steel against corrosion [24]. The Type 430 stainless steel specimen that was layer-by-layer coated with a 65-nm-thick aluminosilicate layer exhibited an extremely high (i.e., >1.0 V vs. Ag/AgCl) pitting potential in 0.6 mol dm^{-3} NaCl solution. This potential was significantly higher than that (<0.2 V vs. Ag/AgCl) of a single-layer coating of the same thickness; the single-layer coating had a pitting potential comparable to that of the non-coated stainless steel. The improved corrosion resistance stemming from the layer-by-layer aluminosilicate coating was also demonstrated by performing a cyclic corrosion test, consisting of 30 cycles of salt spray, drying, and wetting [24].

In this study, the aluminosilicate layer-by-layer coating on Type 430 stainless steel was characterized in detail in order to elucidate the mechanism governing the improved corrosion resistance offered by the coating.

2. Experimental

2.1. Coating preparation

Amorphous aluminosilicate films were prepared from mixed precursor solutions of tetraethoxysilane (TEOS) (Kanto Chemical) and aluminum *sec*-butoxide ($Al(O^sBu)_3$) (Kanto Chemical) by multiple spin casting on Type 430 stainless steel, mirror-finished by electrochemical-mechanical polishing. Details of the spin casting and the preparation of precursor solutions are provided elsewhere [24]. Briefly, precursor sol solutions with an atomic ratio of Al/Si = 20/80 and total Al + Si concentrations of 50, 100, and 500 mmol dm^{-3} were spin-coated onto a stainless steel substrate at 3000 rpm for 20 s, by a Mikasa 1H-D7 spin coater. The coated specimen was exposed to hot air (Iuchi hot gun) for 120–240 s to promote hydrolysis of the deposited gel layer; the substrate was then cooled to room temperature by the blowing of cold air for 20 s. The occurrence of hydrolysis was verified by the wetting behavior of the surface during the spraying of water droplets. These cycles of spin coating, heating, and cooling were repeated 10, 5, and 1 times for the 50, 100, and 500 mM precursor sol solutions, respectively, thereby resulting in ~65-nm-thick coatings. The former two coatings are classified as a layer-by-layer coating and the last one as a single-layer coating. The resulting gel films were annealed in air at 400 °C for 1 h. Prior to coating, the precursor sol solutions were aged for 24 h at an ambient atmosphere to control the viscosity.

2.2. Coating characterization

Surfaces of the coated specimens were examined by using JEOL JSM-6500F and Zeiss Merlin field emission scanning electron microscopes operated at 10 kV and 1.5 kV, respectively. Furthermore, EBSD results of the uncoated stainless steel surface was analyzed by using a TSL OIM system. The coated and samples were subjected to a cyclic corrosion test consisting of 30 cycles of spraying 5% NaCl solution at 35 °C for 2 h, drying at 60 °C for 4 h, and wetting at 50 °C and >95% relative humidity for 4 h. Cross-sections near the scratched regions were observed and analyzed by a Hitachi, HD-2000 scanning transmission electron microscope equipped with energy dispersive spectroscopy (EDS) facilities. The electron transparent cross-sections were prepared using a Hitachi, FB-2100 focused ion beam (FIB) system. The surface of the coated specimens was also examined by a SII, SPA-400 c-AFM system. A Rh-coated Si conductive probe was used to obtain I-V curves, as well as current and topographic images of the surfaces.

Moreover, a microcapillary cell with a tip diameter of 450 μm was used for the electrochemical characterization of the coated surface by separately examining the flaw-free and flaw-containing regions. Potentiodynamic anodic polarization was performed at a potential sweep rate of 20 mV min^{-1} from the corrosion potential by affixing the cell filled with 3.5% NaCl solution to the coated specimen surface. The microcapillary cell consisted of an Ag/AgCl/3.5% NaCl reference electrode and an Au wire counter electrode.

3. Results and Discussion

3.1. Surface and cross-sectional observations

The ~65-nm-thick aluminosilicate coatings obtained from spin casting 50, 100, and 500 mmol dm^{-3} precursor solutions in 10, 5, and 1 cycles, respectively, all had an Al/Si atomic ratio of 25/75, as reported previously [24]. The specimen surfaces with and without coating after thermal treatment in air at 400 °C (Fig. 1a and b, respectively) were examined via SEM and the micrographs revealed grain orientation-dependent features; i.e., in both cases, fine nodules are densely dispersed on some grain surfaces, but only sparsely on others. The nodules developed during the thermal treatment at 400 °C, owing to thermal oxidation of the stainless steel. This indicates that thermal oxidation occurs even in the presence of the ~65-nm-thick aluminosilicate coating, which is apparently an inadequate barrier to gas diffusion. In addition, nodules form irrespective of the concentration of the precursor solutions from which the coatings are formed.

The grain orientations on which high densities of nodules form were identified via EBSD analysis. Fig. 2 shows a scanning electron micrograph (Fig. 2a) and the corresponding EBSD inverse pole figure map of the uncoated 400 °C-thermally treated specimen. As the map shows, a high density of fine nodules form on the surface of grains with the {111} orientation, which has the lowest atomic surface density; in contrast, a significantly lower density of nodules forms on the {100} grain, which has the highest atomic surface density. The mechanism of the grain orientation-dependent formation of oxide nodules, although interesting, is beyond the scope of this study. Since similar nodules form on the coated specimens, the surface of the coated specimen was examined via c-AFM.

Fig. 3 shows topographic and current images of the surface coated from the 50 and 500 mmol dm^{-3} precursor solutions. The topographic images (Fig. 3a and c) reveal the presence of similar nodules on both the surfaces. The size of the nodules is several 200–300 nm (diameter) × 3–4 nm (height) in average. When the current image was measured by applying a bias voltage of +10 V to a conductive probe with respect to the stainless steel substrate, there was a high current (100 nA) flow at the nodule sites, as shown by arrows in Fig. 3b and d. The extremely low current in the surrounding regions indicates that these areas are highly insulating.

The nodules formed by the oxidation of the stainless steel substrate are directly observed by the TEM. Fig. 4a shows a

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