Preparation And Corrosion Studies Of Self-Healing Multi-Layered Nano Coatings Of Silica And Swelling Clay

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Abstract
The investigation of self-healing ceramic coatings is of great importance in many critical applications. We have investigated the feasibility of self-healing coatings which automatically repair the damaged part by physical and chemical reaction. In particular, we have focused on swelling clay (hectorite), which expands cubically and blocks the reactants from the substrate. In this study, we have tried to deposit clay and silica multi-layers using the spin coating technique. These coatings are analyzed using SEM, EPMA, AFM and a laser microscope for their features. Finally, fractal analysis has been carried out to confirm the micrographs taken by laser microscope after corrosion test.

Keywords
Self-healing Multi-layer Silica Swelling clay Corrosion phenomena

Introduction and previous work
Smart composite materials have attracted much attention in recent years [1, 2, 3]. These desirable materials which possess various properties, for example self-reactivity for external impulse and protection from the harsh environments, are necessary for future technology based industries. Various self-healing techniques are used to increase the life of the composite and to provide reliability. The techniques are: dispersion of self-healing capsules and thermally reversible reactions of some specific polymers [1, 4]. Because of their simple healing mechanisms, they have a wide variety of applications that are expected in multiple material fields [1—8].

Ceramic coatings for substrates not only function to protect the surface but also to provide additional properties like anti-reflection and a gas barrier. However, if the coatings are damaged and/or pinholes formed, serious damage could occur due to the corrosion over and in the substrate. For this reason, hard, tough films are being developed using inorganic-organic composite materials [9, 10, 11, 12].

The main objective of this paper is to evaluate the characteristics of multi-layered coating films composed of swelling clay (hectorite) and silica. The clay belongs to the smectite group with a layered structure that has cations in the interlayer space. It is shown that the swelling properties of clay minerals come from the hydration of cations in the interlayer space [13]. Because of swelling, the clay minerals exhibit a specific viscosity called thixotropy. This property has the blocking effect against the dissolved ions in the water inside the cavities. Keeping this property in mind, this clay is utilized as a barrier or sealing material for radioactive disposal. If we can incorporate this property into the coating materials, we will be able to protect the substrate even when the coating films are damaged by cracks and pinholes.

In this paper, we discuss multi-layer composite coatings of SiO2 and swelling clay (synthesized hectorite) produced by the spin coating technique. We investigate the structure and the corrosion phenomena of the multi-layered composite coatings formed on glass and stainless substrates under various conditions.

Experimental
Preparation
Two kinds of sols were prepared in order to obtain silica and clay coatings. The silica sol was prepared from tetraethoxysilane (TEOS, 98%; Wako Pure Chemical Industries, Ltd., Osaka, Japan), H2O and EtOH in the presence of HCl (35%; Wako Pure Chemical Industries, Ltd., Osaka, Japan) catalyst. The stoichiometry of homogenous solution (TEOS: 10.82H2O: 0.69EtOH: 0.024HCl) was allowed to react in a beaker at 40 °C for 1 hr. The clay sol was prepared with synthesized hectorite (Wako Pure Chemical Industries, Ltd., Osaka, Japan), which was suspended in the water under ultrasonic irradiation. Clay sols of various concentrations were prepared and a 1.3 wt% clay sol selected for this experiment. The sol was semi-

Fig. 1. Our conceptual design for self-healing coating in the adverse environment (Silica, clay layered composite)
translucent. The dimension of the glass substrate (Matsunami Glass Ind. Ltd) for coating was maintained at 30×30×0.12mm. The substrate was cleaned in ethanol under ultrasonic irradiation and then spin-coated in air. The multi-layered coatings were deposited using silica and clay sols. The spinning time of the silica and clay coating was maintained at 5 and 1 sec., respectively, with a rotation speed of 1000 rpm. Then they were heated on the hot plate during each stage at a temperature of 110 °C for 5 min. The stainless steel substrates were also coated to analyze the corrosion protection of the multi-layered coating. Unpolished SUS430 plates (20×20×0.3mm) were cleaned in ethanol under ultrasonic irradiation before they were coated by a spin coating technique under the same conditions as the glass substrate.

Characterization
The films were characterized for the surface structure and adhesion property by using a scanning electron microscope (HITACHI S-5000, 20kV). To find out the best preparation conditions, the surface of the structure was observed using a Contact-Mode Atomic Force Microscope (Digital Instruments, J-Scanner). To make drafts of these images, we used Digital Instruments and Nanoscope Ea software. The contact angle of the water droplet on the first silica layer was measured based on JIS R 3257. The thickness of the silica coating on the stainless substrate was measured with a confocal laser microscope (KEYENCE VK-9500, λ=408nm). The wavelength dispersive spectrometry (WDS) analysis was carried out with a JEOL JXA-8800 scanning electron microscope after corrosion tests. The samples were coated with gold to analyze with the same. The acceleration voltage was maintained at 10 kV.

Corrosion test
The corrosion tests were performed for the multi-layered coatings on stainless steel substrates. The multi-layer coated steel substrate was scratched crosswise with a sharp knife-edge (the width of scratch ~100µm). After this operation, the scratched substrates were dipped into the 5.0 wt% sodium chloride solution. The solution in these containers was evaporated in an oven at 50 °C for 24 hr. Then these substrates were washed gently with distilled water to remove the precipitated sodium chloride crystals and corrosion residues, and finally dried again at 50 °C. These stages were repeated up to 7 times. The surfaces of the substrate were observed by the laser microscope.

The corrosion index was estimated with the fractal analysis technique for each corrosion test [14]. For this study, the optical micrographs were digitized with a size of 1024×1024 pixels. This method computes the number of cells required to entirely cover an object, with grids of cells of varying size. It is performed by superimposing regular grids over an object and by counting the number of occupied cells. The logarithm of

Fig. 2. The cross sectional SEM image of multi-layered coating film with silica and clay. (a) silica-clay-silica, (b) silica-clay silica bi-coating

Fig. 3. AFM images of (a) glass substrate, (b) first silica layer on the substrate, (c) clay on the first silica layer, (d) second silica on the clay layer
N(r), the number of occupied cells, versus the logarithm of (1/r), where r is the size of one cell gives a line whose gradient corresponds to box (fractal) dimension. These images were converted to monochromatic images for clarity. For the sake of comparison, 40 points of the fractal dimensions were plotted against the number of corrosion tests.

**Results and discussion**

Our conceptual model for self-healing is shown in Fig. 1, where Fig. 1a shows alternative cracked silica and clay layered composites. When this kind of situation exists in a corrosion environment, the clay layers absorb the corrosion media and swells by itself. In Fig. 1b, the expanded hectorite clay shows that it has filled the cavity by absorbing the corrosion media. This filling effect of clay layers may protect the substrate from the corrosion media.

Figure 2 shows the cross-sectional image of the multi-layered coating using SEM. Figures 2a and 2b depict multi-layered coated substrates with one and two alternate layers of clay, respectively. The thickness of the silica layer is varied between 350—500 nm, and the clay layer is between 250—330 nm. The lower-most silica layer deposited on the glass plate is well intact. The interface between them looks excellent. Neither de-lamination nor a crack is observed at the silica layer or at the interface between silica and clay layers. The fracture in the clay layer is observed due to the rupture, which is shown in Fig. 2. The fracture morphology of the clay layers are oriented horizontal to the substrate, which are sandwiched between silica layers. This clay layer orientation is due to the crystal structure and resultant anisotropic morphology of clay mineral. The control of the thickness of the healing layer (clay layer) is also important, because it has a strong effect on the crack size to be healed. The thickness of the clay layer can be controlled in the range of 150—300 nm by changing the duration of the spin coating.

The topological profiles of each coating surface observed using AFM, are shown in Fig. 3. From this observation, the surface structure seems to play an important role in determining the thickness of the coating layer and the surface structure of the coating. Figure 3a shows the topological profile of the as-received glass substrate with small irregularities and wave shaped images, which are intrinsic to the glass sheet production process. Figure 3b represents the surface image of the first silica layer that was coated on the glass substrate. It shows a smoother surface than the glass substrate. Figure 3c shows the surface structure of the first clay layer that is formed on the first silica. The scanned AFM image did not show any fractures on the clay layer. The clay-coated surface showed asperity. The Ra of 1.92 is 10 times higher than that of the first silica layer (Ra=0.15). Figure 3d shows the second silica layer over the clay layer. In spite of the varying roughness of the clay layer, the surface of the silica layer is as flat as the first silica layer surface.
This observation implies that the roughness observed for the clay layer has no effect on the next silica layer.

For the purpose of the corrosion resistance test, the multi-layered coating over the stainless substrate is investigated. Usually, these coating films are transparent and the thickness of the first silica layer on the stainless substrate is 1.7 ~ 1.8 µm. This is measured using a laser microscope. The thickness of the first silica layer on stainless steel substrate is three times thicker than on the glass substrate. In addition, it is possible to predict the difference of the coated silica surface on both the glass and stainless steel silica layer. The contact angles of silica coated on glass and stainless steel substrates are denoted as substrates by the contact angle measurement. This difference affects the multi-layered coating over the ò=26.8±1.53° and ò=27.9±0.73°, respectively. Considering the same chemical properties of the coating on the above-mentioned substrate, the fine difference of the contact angle is attributed to the roughness of the surface.

A corrosion test is very important to demonstrate the protection properties of the coating. This effect is improved by the self-healing behavior that is attributed to the swelling clay layers. Here, we report the qualitative results of the corrosion tests conducted on the raw and coated surfaces. The results of the corrosion test are shown by 3D topological images taken by the laser microscope in Fig. 4. The uncoated stainless steel surface is exposed to the corrosion environment as shown in Fig. 4a, with red rust on the surface. Figure 4b shows the stainless steel substrate coated with silica. Though some corrosion products were partially observed, this coated surface is largely protected from corrosion. Figures 4c and 4d show the corrosion test results for the silica-clay-silica coating, and the silica-clay-silica bi-coating surface, respectively. In both cases, the surface layers exist with small corrosion deposits. Both Figs. 4c and 4d exhibit surface layer peeling off at different areas of the surface. The mechanical strength of the silica layer on the clay is weak [15]. Because of the poor strength of the silica layer over the clay, it is easily broken by the residual stress caused by the sodium chloride crystal growth. The swelling clay that was broken by the scratching remained on the stainless steel surface. For this reason, the stainless steel substrate was protected against the attacking ion. Though we are not able to directly observe the swelling reaction, it is concluded from the careful observations of Fig. 4 that this clay is good for the protection of the substrate. The improved corrosion resistance was observed for the multi-layered coating with the swelling of double clay layers (Fig. 4d). The present multi-layered coatings formed by silica and clay layers were considered to have the capability to heal the cracks by the swelling of the clay layers.

To identify the clay layers in the scratched areas, EPMA studies were carried out on the corroded surface of each specimen. The amount of clay present in the scratched area is known indirectly by the silica of each specimen. The SEM images as well as the line plots of the clay layers are shown in Fig. 5. In Fig. 5a, the silica content is nil compared to other specimens with coatings. In the second image (Fig. 5b), the silica content at the scratched areas is almost zero. Figures 5c and 5d show the multi-layered coatings of single and double clay layers coating. The amount of clay present in the scratched area is known indirectly by the silica content of the line plots.

The corrosion surface was analyzed using fractal analysis to determine the progression of the corrosion over the surface. This box-counting method relies on digitized representations of the objects of interest and will be affected by their resolution. As explained in the experimental procedure, the fractal dimensions, varying with box size, are used in the analysis. The fractal dimension plotted against the number of corrosion tests for non-coated and multi-layered coatings, are shown in Fig. 6.

At the non-coated stainless substrate (Fig. 6a), the average of the fractal dimension was increased drastically with a wide range of variation. After the third corrosion test, the fractal dimensions reached their maximum. The surface was fully covered with corrosion products. In the silica-coated stainless steel substrate (Fig. 6b), the surface without a corrosion test and the first test had a similar effect on the average fractal dimension. By increasing the number of tests, it was found that the fractal dimension was increasing gradually. The silica-clay-silica (Fig. 6c) and silica-clay-silica bi coating (Fig. 6d) show similar behavior. After the first test, the fractal dimension was changed and was widely varied. This variation is mainly regarded as the partial peeling of the surface coating. The edges of the peeling part or the residue of the corrosion products on these parts, after washing, was counted during the analysis. On the whole, the range of the error bars was narrow as the corrosion tests were repeated. The behavior of the fractal dimensions tend to maintain or decrease. It was concluded from these results that the average of the fractal dimension is useful to indicate the behavior of the corrosion, and as some corrosion generates randomly, it is important to estimate the tendency by the number of data collections.

**Conclusion**

The multi-layered coating has been investigated based on the proposed self-healing or repairing concept. To check this property in the solution environments, the swelling clay was inserted into the silica layers. The multi-layer coating of silica and swelling clay was prepared by the spin coating technique. By repeating this coating process, various multi-layered coatings with different combinations of silica and clay layers were successfully fabricated. From the corrosion phenomena of multi-layered coating with the scratched cracks, the healing effect was not revealed directly; however, the protection by the swelling clay was confirmed. The fractal dimensions for the coating surface could be used to understand the phenomena of the corrosion.
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References

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