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Preparation of Multi-Layered Self-Healing Coating by Using Silica and Swelling Clay

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Research in nano ceramic coating materials, which is conjugated with intelligence, is of great importance in many critical applications. Ceramic coating for the substrate has high-level protection, however, once the coatings is degraded, both coating as well as the substrate are severely damaged by corrosion. We have investigated the feasibility of self-healing coatings which automatically repair the damaged part by chemical reaction, and focused on the swelling clay. By swelling from the solution, this clay expands cubically which blocks the water and dissolved ions. In this study we tried to prepare a multi-layer coating of SiO_2 and swelling clay under various conditions by spin coating technique. As the result, it was shown that the clay layers controlled the thickness were interposing with repetition of the coating. The thickness, surface condition, and the corrosion phenomena were studied for this coating.
Key words: self-healing, multi-layer, silica, swelling clay

1. INTRODUCTION

Smart composite materials have attracted much attention in the recent years [1, 2]. These desirable materials offer certain advantages and the name intelligent materials come from sensing and integrating the properties. Various self-healing techniques are used to increase the composites life duration. The techniques are for example; the dispersion of self-healing capsules [1] and the thermally reversible reaction of some specific polymers [4]. Because of their simple healing mechanisms, there are wide varieties of applications, which are expected in the multiple material fields [1-5].

Ceramic coatings for substrates have not only the function to protect the surface but also to provide additional properties; for example anti-reflective coatings. But if the coatings are damaged by cracks or pinholes, serious damages can be possible due to corrosion over and in the substrate. On this reason, hard and touch films were developed using inorganic- organic composite materials [6-9].

The main objective of this paper is to evaluate the structure and properties of multi-layered coating films by swelling clay mineral, hectorite. It has been shown that the swelling properties of clay minerals come from the hydration of cation in the interlayer space [10]. As a result of swelling, the clay minerals show specific viscosity so called thixotropy. This property has the blocking effect against water and dissolved ions in the water. This swelling function work as the sensor which blocks further water and dissolved ions intake in to the broken cavities. If we can incorporate these properties in to the coating materials, we will be able to protect the whole substrate composition even the coating films are damaged by cracks and pinholes. Fig. 1 illustrates our conceptual model for self-healing.

In this paper, we prepared a multi-layer coating of SiO_2 and swelling clay (synthesized hectorite) under various conditions by spin coating technique. The thickness of this coating film was mainly controlled by rotation speed and running time during the spin coating and the condition of sol solution; viscosity or the degree of hydrolysis reaction. Under various conditions, we investigated the structure and corrosion properties for the multi-layered coatings formed on the flat glass substrate. Furthermore, this coating was also formed on the stainless steel; the corrosion behavior of these substrates was evaluated using sodium chloride (NaCl) solution. This test condition, which is a coastline environment base, was executed with wet and dry process under heat-retention. Consequently, the multi-layered coatings fabricated by above-mentioned multi coating method was found to exhibit better corrosion resistance.

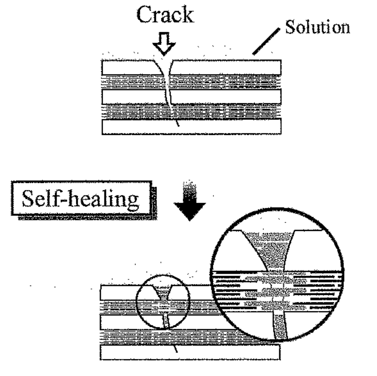

Figure 1. Conceptual model of self-healing mechanism.

2. EXPERIMENTAL PROCEDURE

2.1 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), H_2O and EtOH in the presence of HCl (35%; Wako Pure Chemical

Industries, Ltd., Osaka, Japan) catalyst. The stoichiometry of homogenous solution composition of TEOS (10.82 H_2O: 0.69 EtOH: 0.024HCl) was treated in a beaker 40 °C for 1 hour. The clay sol was prepared by synthesized Hectorite (Wako Pure Chemical Industries, Ltd., Osaka, Japan), which was suspended in the water under ultrasonic irradiation. The clay sol of various concentrations was prepared and out of which 1.3 wt% clay sol was selected for this experiment because of its feasibility. The sol was semi-translucent. The sol was semi-translucent. The dimension of glass substrate (Matsunami Glass Ind. Ltd) for coating was 30x30x0.12mm. The substrate was cleaned in the ethanol under ultrasonic irradiation and then spin-coated in the air. These multi-layered coating was fabricated by silica and clay sols. The spinning time of silica was 5 sec and for clay 1 sec with rotation speed 1000rpm, to get the multi-layer structure, they are heated on the hot plate at each stage. Heat treatment was performed on the hot plate at a temperature of 110°C for 5 minutes. The stainless steel (SUS 430, 20x20x0.3mm) substrates without polishing are cleaned in ethanol under ultrasonic irradiation before they are coated by spin coating technique at the same conditions, which were selected on the glass substrate. The films are characterized for the surface structure and adhesion property by scanning electron microscope (HITACHI S-5000, 20kV). To find out the better preparation conditions, the surface of the structure was observed using Contact-Mode Atomic Force Microscope (Digital Instruments, J-Scanner). To make drafts of these images, we have used Digital Instruments, Nanoscope Ea software. The hardness of obtained coating was characterized by the ultra micro indentation system (CSIRO, UMIS- 2000) using indentation load up to 10 mN.

2.2 Corrosion Test

The corrosion tests are performed with stainless steel. The multi-layer coated steel substrate was crosswise scratched with a sharp knife-edge (the width of scratch: ca. 100 μm). After this operation, the scratched substrates were laid in the uncovered plastic containers, and they were dipped into the 3.0 wt% sodium chloride solution. The solution of these containers was evaporated at 50°C in the oven, and then the substrates were washed with distilled water and dried at 50°C. These stages of operation were repeated 7 times. The surfaces of the substrate were then observed by the optical microscope.

3. RESULTS AND DISCUSSION

3.1 Coating on the glass substrate

Fig. 2 shows the SEM cross-sectional image of the multi-layered coating film. The thickness of silica layer was varied in between 350 to 500 nm and the clay layer was between 250 to 330 nm. The lower most silica layer deposited on the glass plate was very well intact, that the interface between them looks excellent. Ether delamination or crack was not observed at the silica layer and the interface between silica and clay layers. The fracture at the clay layer was observed due to the rupture not by delamination, which is shown in Fig.2. Making an allowance for the morphological fracture, it was also suggested that the clay layers sandwiched by

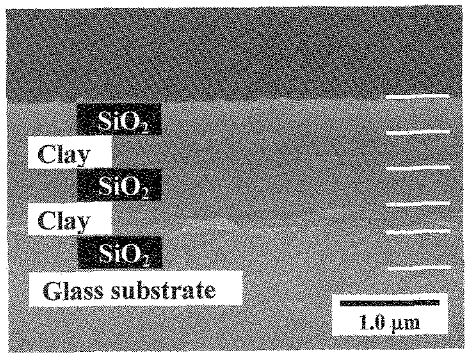

Figure 2. The sectional SEM image of multi-layered coating film by using both silica sol and swelling clay sol.

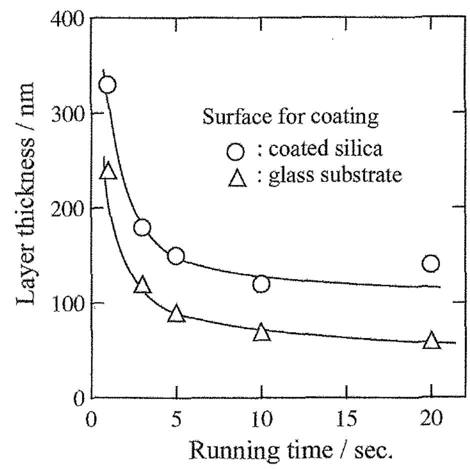

Figure 3. Running time in the spin coating versus layer thickness of the clay on the different surface for coating.

silica layers were oriented to the substrate. This orientation is owing to the crystal structure of clay mineral. In general, it pretends that the morphology like this causes the property of water stop, namely by preventing the diffusion of a variety of the ion and adsorption.

The control of the thickness of healing layer (clay layer) is important, because it has strong effect on the crack size to be healed. The multi-layered coatings are prepared under various conditions. The thickness of the clay layer can be controlled by the concentration of coating sol, rotation speed, running time and surface structure of the substrate. In the present study, the effect of running time on the spin coating was mainly concentrated for modifying the thickness. The control of the thickness of clay layer is important for healing property, because the healing size is believed to be directly related to the thickness of the healing layer. Fig. 3 shows the relationship between the layer thickness and the running time, when the clay layer was coated on both glass and silica layer coated on the glass. In this experiment, the running (spinning) time was changed in between 1 to 20 sec. As shown in Fig. 3, the clay layer thickness was drastically decreased with increasing the running time. And the clay layer coated on silica surface was from 1.2 to 2 times more thick than that coated on the virgin glass. This effect could be due to the fact that the glass substrate surface has low retention due to the improved hydrophilic by the ethanol cleaning. From the result, it is understood the thickness of the clay layer on the silica surface can be controlled in between 150 and 300 nm by changing the running time. It should be noted that the present clay sol was able to coat the clay layer without any problems. To obtain more thick clay layer, the above said process should be repeated.

Fig. 4 indicates the topological profiles of each coating surfaces. From this observation, the coating seems to play an important role to determine the thickness of the coating layer and the surface structure of the coating. Fig. 4a shows the topological profile of the glass substrate with small irregularities, which are formed during the glass sheet production processes. Fig. 4b represents the surface image of the first silica layer coating that was coated on the glass substrate, and it shows more un-striated surface than glass substrate. This surface structure change is believed to affect the retention of clay sol, and the thickness difference of the clay layer (Fig. 3). Fig. 4c shows the surface structure of the first clay layer coating surface which is formed on the silica layer coated on the glass. The scanned image with AFM probe didn't show any fracture on the clay layer. The clay-coated surface shows asperity, the maximum depth was 10 times higher than that of the first coated silica. Fig. 4d shows the second silica layer over the clay coating. In spite of the roughness of the clay layer, the surface of the silica layer as flat as the first silica surface (Fig. 4b). This observation implies that the roughness observed for the clay layer can be decreased by sufficiently altering the silica coating. In the wide scan range (50x50μm), the similar surface structure was revealed and no defect was observed.

Table I presents the hardness and the penetration depth for the coating formed on the glass substrate. The hardness of the first silica on the glass substrate was increased as the load was increased. The indentation was affected by the glass substrate, because the penetration depth was larger than the coating thickness. The hardness of the first clay coating (SiO_2-Clay) shows the lower value compared to the first silica and the same way the hardness of the second silica layer (SiO_2-Clay-SiO_2), too. This result was denoted that the top coating was directly impacted into the soft undercoat, and then this multi coating needs heat treatment in order to improve the strength. Because the heat treatment increases the condensation of the SiO_2 coating and the desired interface of SiO_2-Clay will be formed by this treatment.

3.2 Coating on the SUS 430 substrate

Corrosion test is very important to demonstrate the protection properties of coating and this effect is improved by the self-healing behavior that is attributed to the swelling of the clay layers. The results of the corrosion test are shown in Fig. 5. In Fig. 5a, the non-coated stainless steel surface is exposed after treatments. The red rust is observed in the whole surface as seen in this figure. Fig. 5b shows the sample of silica surface coated on the stainless steel. Small deposits are observed on the coating and some deposited corrosion products are also observed in the scratched line. Along

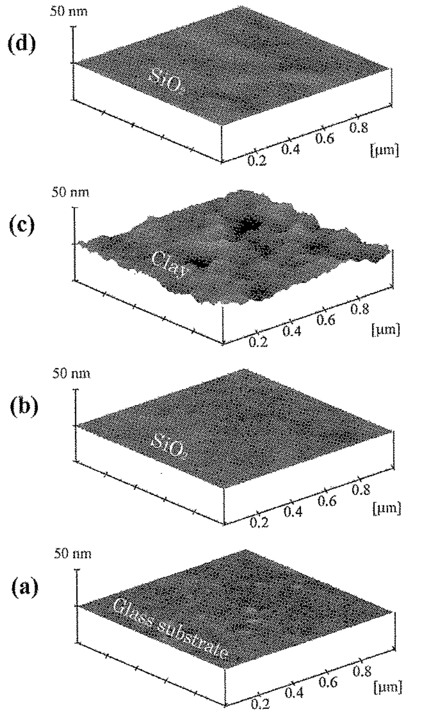

Figure 4. AFM images of (a) glass substrate, (b) coated first silica on the substrate, (c) coated the clay on the first silica, (d) coated the second silica on the clay.

Table I. Hardness and Adjusted total penetration depth determine by nanoindentation.

	Glass substrate		SiO_2		SiO_2-Clay		SiO_2-Clay-SiO_2	
	GPa	nm	GPa	nm	GPa	nm	GPa	nm
1 mN	8.83	81.5	2.87	133.2	1.12	200.3	1.30	203.1
2 mN	8.12	125.9	2.85	192.9	1.33	265.6	1.42	276.0
5 mN	7.40	212.3	3.50	296.4	2.12	350.2	1.91	390.9
10 mN	7.47	306.6	3.98	419.0	2.79	450.5	2.29	517.8

the knife-edge line the corrosion has proceeded and the coating was peeled off close to the line. Fig. 5c and 5d shows the corrosion test results for the silica-clay-silica coating, and the silica-clay-silica bi-coating surface, respectively. These coated surfaces have better protection than the silica only surface some corrosion products are accumulated at the peeling parts of the coating. Based on these results for the silica coated on the clay surface, the silica layer is concluded to be inefficient. The clay was oriented horizontally and then the silica layer coated on the clay is apt to fall off from the surface. The deposits were also observed on the scratched lines. The multi coating have double clay layer shows the better protection at the scratched edges part than other coating cases. In this experiment, the crack size introduced by a knife-edge is too large compared with the film thickness. The scratched edge parts are also affected by the solution including water and the attacking ion.

There is a possibility that the broken clay parts formed during the scratching remains at the edge of cracks. Though we are not able to observe directly the swelling reaction, it is concluded from careful observations in Fig. 5 that the improved corrosion resistance observed for the multi-layered coating with

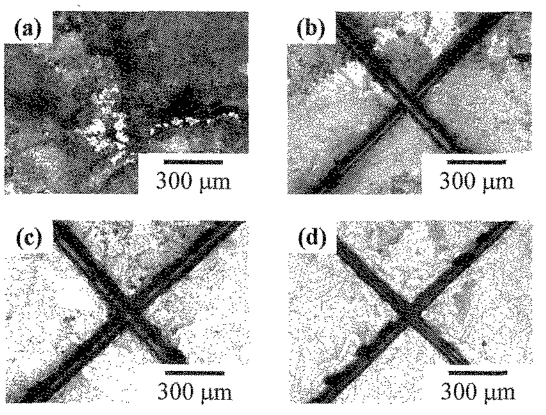

Figure 5. Optical micrograph of the corrosion tested surfaces at the 7 times. (a) non-coated, (b) silica coating: condition 1, (c) silica-clay-silica coating: condition 1and 2, (d) silica-clay-silica bi-coating. Black spots present corrosion products.

the double clay layers (Fig. 5d) is caused by the swelling of both the clay layers and the broken clay parts within the scratched cracks. In conclusion, the present multi-layered coatings formed by silica and clay layers have good capability to heal the cracks by the swelling of the clay layers.

4. SUMMARY

The feasibility of multi-layered self-healing coatings has been investigated according to the proposed multiplayer coating concept. In this, the swelling clay is inserted into the coating layers for adding the self-healing property. The multi-layer coating of silica and swelling clay was prepared by spin coating. By repeating this coating process, various multi-layered coatings with any combination of silica and clay layers are successfully fabricated. The thickness of the clay layer in the multi-layered coatings was controlled by adjusting the running time of the spin coating. The mechanical properties of the multi-layered coating are proved to be affected strongly by the coated layer. From the results of the corrosion test for the multi-layered coatings with the scratched cracks, the healing effect was not revealed directly, however, the protection by the swelling clay was confirmed.

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