Investigation of structure of a thin SiO₂ layer as an antifouling and corrosion-resistant coating

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The structures of a SiO₂ layers synthesized using perhydropolysilazane [PHPS, labeled as SiO₂(PHPS)] on both Si and Fe/Si substrates were studied using Fourier transform infrared spectroscopy (FT-IR) and neutron reflectivity (NR) analysis. The FT-IR results revealed that no unreacted PHPS remained and that the primary component of the SiO₂(PHPS) layer could be considered to be SiO₂. The NR analysis suggested that a uniform SiO₂(PHPS) layer was synthesized on the Si and Fe/Si substrate and that the density of this SiO₂(PHPS) layer was lower than that of natural SiO₂. In addition, the density of the SiO₂(PHPS) layer was altered by varying both the thickness and the type of substrate used. These results indicated that the variation in the density of the SiO₂(PHPS) layer depended on the efficiency of cross-linking reaction between the silazane oligomers in the PHPS coating.

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1. Introduction

Si-based ceramics have been studied as coating materials to protect certain components from dust, dirt, and moisture.¹⁾ Perhydropolysilazane (PHPS) is a promising material for use in the protection of metallic materials in corrosive environments; this is because PHPS can be easily used to synthesize high-quality SiO₂ layers on metallic materials through the hydrolysis or oxidation of PHPS.^{2),3)} However, one major concern regarding the use of such Si-based materials is that the formation behavior of the SiO₂ layer may change depending on the surface or condition of the material protected by the PHPS layer. Therefore, it is essential to thoroughly investigate both the structure and the formation mechanism of the synthesized SiO₂ layer.

We used PHPS to synthesize a waterproof SiO₂ layer, denoted as SiO₂(PHPS), for the magnetic alloy core of the accelerator ring in the Japan Proton Accelerator Research Complex (J-PARC), Tokai, Japan; the core is primarily composed of Fe.⁴⁾ The amount of iron rust decreased with an increase in the thickness of the SiO₂(PHPS) layer in the salt-spray test (Fig. 1), that is, the waterproofing property of the SiO₂(PHPS) layer increased with an increase in its thickness. However, the level of stress in the SiO₂(PHPS) layer also increased, and this can lead to cracking. Therefore, we evaluated the thickness of the SiO₂(PHPS) layer and concluded that thicknesses of 100–1000 nm were optimal with respect to its waterproofing properties and cracking resistance. However, the correlation between these properties and the thickness of SiO₂(PHPS) layers remains unclear.

A variety of techniques have been used to study the structure of thin SiO₂ layer, including Fourier-transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy, atomic force microscopy, and reflectometry.^{5)–8)} In particular, the neutron

Fig. 1. Relationship between SiO₂ layer thickness and the corrosion rates under the salt-spray test.

reflectivity (NR) technique is ideally suited to study the structures of thin layers on various surfaces and interfaces.^{9),10)} The thickness, density, and roughness of thin SiO₂ layers can be evaluated by the NR technique. Therefore, in this study, we prepared two types of samples, namely, a thin SiO₂(PHPS) layer on a Si substrate [SiO₂(PHPS)/Si] and a thin SiO₂(PHPS) layer on an Fe/Si substrate (thin Fe layer between the SiO₂(PHPS) layer and the Si substrate [SiO₂(PHPS)/Fe/Si]). Then, using the NR technique, we analyzed the structures of these samples to determine the thicknesses, densities, and roughnesses of the SiO₂(PHPS) layers. Subsequently, we also discussed the formation mechanism of the SiO₂(PHPS) layers on the basis of the structural parameters obtained through the NR analyses.

2. Experimental procedure

2.1 Sample preparation

The Si wafers (diameter = 5.08 cm, thickness = 0.3 mm) and PHPS polymer (AQUAMICA) were supplied by SEMITEC Co. Ltd. (Tokyo, Japan), and AZ Electronic Materials Co. Ltd. (Tokyo, Japan), respectively; these materials were used without further purification. Owing to the rough surface of the actual magnetic alloy core, the NR technique could not be used on the core itself. Therefore, we studied the structures of the SiO₂(PHPS) layers by preparing and using model compounds. Since Fe is the main component of the magnetic alloy core, the Si

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wafers that were deposited of the thin Fe layer on the substrate surface were prepared as the model compound. We prepared the Fe/Si substrates using a sputtering system installed at the AIST Nano-Processing Facility. Using a spin-coater (MS-A150, Mikasa Co. Ltd., Tokyo, Japan), the SiO₂(PHPS) layers were prepared by spin coating 5% of PHPS/*p*-xylene solution at a speed of 6000 rpm. Subsequently, the samples were cured at 60°C for 1 h and allowed to stand for 48 h at 20°C. The thin and thick SiO₂(PHPS)/Si samples (in this paper, these samples are denoted as type-A and type-B, respectively) and the thin and thick SiO₂(PHPS)/Fe/Si samples (denoted as type-C and type-D, respectively) were prepared for the NR measurements. The samples were stored in a box under low-humidity and dust-free conditions at room temperature.

2.2 FT-IR measurement

The samples for the FT-IR spectroscopy analysis were prepared by removing a section from each sample prepared for the NR measurements.

The FT-IR spectra were measured with an FT/IR-4100ST (Nihon Bunko Co. Ltd., Tokyo, Japan) system equipped with an attenuated total reflectance (ATR) unit (PRO670H-S, Nihon Bunko Co. Ltd., Tokyo, Japan). The wavenumber range of the FT-IR spectra was 600–4000 cm⁻¹ and the resolution was 4 cm⁻¹. Each spectrum was determined from the average of 64 scans. All the measurements were performed at room temperature.

2.3 Neutron reflectivity measurements

The NR measurements were performed on a BL17 SHARAKU reflectometer installed at the Materials and Life Science Experimental Facility (MLF) in J-PARC.⁽¹¹⁾ The incident beam power of the proton accelerator was 400 kW for all the measurements. Pulsed neutron beams were generated using a mercury target at 25 Hz, and the NR data were measured using the time-of-flight (TOF) technique.⁽¹¹⁾ The neutron-source to sample distance was 15.5 m, and the sample to ³He gas point detector distance was 2.5 m.⁽¹²⁾ The wavelength (λ) range of the incident neutron beam was tuned to be approximately $\lambda = 2.2\text{--}8.4$ Å using disk choppers. The incident angle was varied from 0.3 to 0.9°, and the exposure times for the measurements at incident angles of 0.3 and 0.9° were 0.5 and 1 h, respectively. The covered Q_z range was $Q_z = 0.008\text{--}0.09$ Å⁻¹, where $Q_z = (4\pi/\lambda)\sin\theta$ (here, θ represents the incident angle). The samples were placed in an Al sample holder on the sample stage, which was installed at the center position of the sample rotation. A 20 mm beam footprint was maintained on the sample surface by using six kinds of incident slits.⁽¹²⁾ All the measurements were performed at room temperature.

The data reduction, normalization, and subtraction were performed using a program installed in BL17 SHARAKU that was developed for the TOF data. The Motofit program⁽¹³⁾ was used to fit the NR profiles using the least-squares approach to minimize deviations in the fit; the thickness, scattering length density (SLD), and Gaussian roughness were evaluated by the program.

3. Results and discussion

3.1 FT-IR analysis of SiO₂ layer

To determine the composition of the synthesized SiO₂(PHPS) layers, the molecular structures of the SiO₂(PHPS) layers were analyzed using FT-IR measurements.

Figure 2 shows the FT-IR spectra of the type-A–D samples in the wavenumber range of 600–4000 cm⁻¹. The absorption of N–H (3400 cm⁻¹) and Si–H (2200 cm⁻¹), which are attributed to

Fig. 2. FT-IR ATR spectra (mean) of the thin SiO₂ layer samples.

unreacted PHPS,^(3),14),15) were not observed in the spectra. This implied that the starting PHPS material completely reacted during the curing reaction. Moreover, the observed FT-IR spectra showed a large absorption peak at around 1100 cm⁻¹. The absorption peak between 1000–1100 cm⁻¹ and the shoulder between 1100–1200 cm⁻¹ were mainly due to absorption by the Si–O asymmetric stretching transverse optical (TO) and longitudinal optical (LO) modes, respectively.^(16),17) In addition, the absorption between 1100–1200 cm⁻¹ was assignable to the stretching vibration of the Si–O bond in the SiO₄ tetrahedral terminal group (SiO₄ terminal).⁽¹⁸⁾ The intensities of the absorption peaks related to the SiO₄ terminal for the type-C and D samples were greater than those of the peaks for the type-A and B samples. As shown in the following sections, the surface roughnesses of the type-C and D samples were greater than those of the type-A and B samples. Therefore, the absorbance of the SiO₄ terminal in both the type-C and D samples was enhanced because of their larger surface area owing to their higher roughness. The absorption peak at around 3300 cm⁻¹ could be attributed to the O–H stretching of the Si–OH group. These results suggested that the synthesized SiO₂(PHPS) material primarily consisted of SiO₂ and similar compounds, as determined from the surface FT-IR measurements.

3.2 Neutron reflectivity analysis of SiO₂(PHPS)/Si

The results of the air-solid reflectivity measurements for the SiO₂(PHPS)/Si samples are shown in **Fig. 3**. The period of the reflectivity oscillations (ΔQ_z) indicates the thickness of the layer (t), while the ΔQ_z value is defined as $\Delta Q_z \approx 2\pi/t$.⁽¹⁹⁾ Because the ΔQ_z value of the type-A sample was larger than that of the type-B sample, the thickness of the SiO₂ layer in the type-A sample was determined to be lower than that of the SiO₂ layer in the type-B sample. The critical wave vector for the total external reflection (Q_c), which is defined as $Q_c = 4(\pi\rho)^{1/2}$ (ρ represents the SLD),⁽²⁰⁾ was observed around $Q_z = 0.01$ (Å⁻¹). Further, the Q_c value of the type-A sample was lower than that of the type-B sample. Assuming that the composition of the SiO₂(PHPS) layer was homogenous, the Q_c value reflected the density of the SiO₂ layer. Therefore, the observed Q_c values indicated that the density of the SiO₂ layer of the type-A sample was lower than that of the SiO₂ layer of the type-B sample.

The NR profiles of the type-A and B samples were analyzed using the Motofit reflectometry package,⁽¹³⁾ and the calculated theoretical reflectivity profiles are shown in Fig. 3. Because a naturally oxidized thin SiO₂ layer was present on the surfaces

Fig. 3. Neutron reflectivity profiles of the type-A (red) and type-B (blue) samples. The circles represent the experimental data, and the solid lines represent the best-fit calculated NR profiles. The insets show the SLD profiles as a function of the layer depth.

Table 1. Best-fit parameters for the reflectivity model data shown in Figs. 3 and 4

		Type-A	Type-B	Type-C	Type-D
SiO ₂ (PHPS)	t (Å)	415	1349	455	675
	ρ ($\times 10^6$ Å ⁻²)	2.09	2.28	1.41	1.79
	σ (Å)	6.60	6.56	17.5	26.0
	ρ_{SiO_2} (g/cm ³)	1.33	1.45	0.89	1.13
Fe ₂ O ₃	t (Å)	—	—	2.24	6.08
	ρ ($\times 10^6$ Å ⁻²)	—	—	6.73	7.85
	σ (Å)	—	—	1.86	2.11
Fe	t (Å)	—	—	91.8	90.3
	ρ ($\times 10^6$ Å ⁻²)	—	—	8.34	8.39
	σ (Å)	—	—	1.94	9.58
SiO ₂ (oxidized)	t (Å)	45.2	22.4	25.1	59.3
	ρ ($\times 10^6$ Å ⁻²)	2.39	2.41	1.71	1.41
	σ (Å)	7.89	2.86	2.10	1.91
Si substrate	ρ ($\times 10^6$ Å ⁻²)	2.07	2.07	2.07	2.07
	σ (Å)	1.87	25.0	1.32	6.66

t : thickness, ρ : SLD, σ : roughness of the surface or interface, ρ_{SiO_2} : density of SiO₂(PHPS) layer as calculated from the ρ value.

of the Si substrates, a two-layer model, SiO₂(PHPS)/SiO₂-(oxidized)/Si, was employed to fit the obtained NR profiles. The symbols represent the observed NR profiles, while the solid lines represent the calculated NR profiles determined from the structural models. The theoretical reflectivity profiles reproduced the experimental NR profiles in the all Q_z -range. **Table 1** shows the structural parameters obtained from this analysis. The t and ρ values of the SiO₂(PHPS) layer of the type-A sample were estimated to be 415 Å and $2.09 (\times 10^6 \text{ Å}^{-2})$, and those of the type-B sample were 1349 Å and $2.28 (\times 10^6 \text{ Å}^{-2})$, respectively. Since the ρ value of natural SiO₂ is $3.47 (\times 10^6 \text{ Å}^{-2})$,²¹⁾ the estimated ρ values indicated that the density of the synthesized SiO₂(PHPS) was lower than either that of natural SiO₂ or that of the unreacted PHPS [with a ρ value of $0.40 (\times 10^6 \text{ Å}^{-2})$] remaining in the SiO₂(PHPS) layer. It was concluded that this change in the ρ value reflected the change in the density of SiO₂ because no unreacted PHPS molecules remained in the SiO₂(PHPS) layer. The ρ value is defined as $\rho = \rho_{\text{SiO}_2} \cdot N_A \cdot \sum_i b_i / M$,²⁰⁾ where ρ_{SiO_2} , N_A , b_i , and M are the density of SiO₂, Avogadro's number, the coherent scattering length of the element, and the molecular weight, respectively. Thus, assuming that the dominant component of the SiO₂(PHPS) layer was SiO₂, the ρ_{SiO_2} values of the SiO₂(PHPS) layers were estimated to be 1.33 (type-A) and 1.45 (type-B), as shown in Table 1. The density of the SiO₂(PHPS) layer, as estimated by the NR analysis, was similar to the density of SiO₂ reported in previous studies.^{22,23)} The density of the

SiO₂(PHPS) layers was altered by varying the thickness of the layers, whereas the conditions for forming the SiO₂ coating were not changed. Therefore, this indicated that the curing reaction of PHPS in the thick layer was more efficient than that in the thin layer. Additionally, the inset in Fig. 3 illustrates the SLD depth profiles for the type-A and B samples, which indicate that uniform SiO₂(PHPS) layers was synthesized on the Si substrates. Therefore, the NR measurements revealed that a uniform SiO₂ layer can be synthesized on a Si substrate by using PHPS and that the density of the SiO₂(PHPS) layer could be altered by varying its thickness.

3.3 Neutron reflectivity analysis of SiO₂(PHPS)/Fe/Si

The air-solid reflectivity measurements for the SiO₂(PHPS)/Fe/Si samples are shown in **Fig. 4**. Since the ΔQ_z value of the type-C sample was greater than that of the type-D sample, the thickness of the SiO₂ layer of the type-C was found to be lower than that of the type-D sample. The Q_c was observed to be around $Q_z = 0.01 (\text{Å}^{-1})$, and the Q_c value of the type-C sample was lower than that of the type-D sample. Assuming that the composition of the SiO₂(PHPS) layer was homogenous, the Q_c values indicated that the density of the SiO₂ layer in the type-C sample was lower than that of the SiO₂ layer in the type-D sample.

The NR profiles of the type-C and D samples were also analyzed using the Motofit reflectometry package, and the calcu-

Fig. 4. Neutron reflectivity profiles of the type-C (red) and type-D (blue) samples. The circles represent the experimental data, and the solid lines represent the best-fit calculated NR profiles. The insets show the SLD profiles as a function of the layer depth.

lated theoretical reflectivity profiles are shown in Fig. 4. Since a naturally oxidized thin SiO₂ layer and a thin Fe oxide layer were present on the surfaces of the Si substrate and Fe layer, respectively, a four-layer model, SiO₂(PHPS)/Fe(oxidized)/Fe/SiO₂(oxidized)/Si, was employed to fit the obtained NR profiles. The symbols represent the observed NR profiles, while the solid lines represent the calculated NR profiles determined from the structural models. For $Q_z < 0.06 \text{ \AA}^{-1}$, the theoretical reflectivity profiles correlated with the experimental NR profiles, whereas the fitting was poor in the $Q_z > 0.06 \text{ \AA}^{-1}$ region. However, as the differences in the high- Q_z region mainly depended on the structure of the Fe layer, the structures of the SiO₂(PHPS) layers could be satisfactorily evaluated using the fitting results. The parameters for the Fe layer obtained in this study were acceptable.²⁴⁾ Table 1 shows the structural parameters obtained from this analysis. The t and ρ values of the SiO₂(PHPS) layer of the type-C sample were estimated to be 445 Å and $1.41 (\times 10^6 \text{ \AA}^{-2})$, respectively, and those of the type-D sample were 675 Å and $1.79 (\times 10^6 \text{ \AA}^{-2})$, respectively. Thus, assuming that the dominant component of the SiO₂(PHPS) layer was SiO₂, the ρ_{SiO_2} value of the SiO₂(PHPS) layers were estimated to be 0.89 (type-C) and 1.13 (type-D), as shown in Table 1. The density of the SiO₂(PHPS) layers estimated by the NR analysis was slightly lower than the density of SiO₂ reported in previous studies.^{22),23)} This demonstrated that the type of coated material used affects the curing efficiency of the PHPS system. However, it also indicated that the curing reaction of PHPS in the thick layer was more efficient than that in the thin layer. The inset in Fig. 4 illustrates the SLD depth profiles for the type-C and D samples, which indicate that uniform SiO₂(PHPS) layers was synthesized on the Fe layers. Therefore, the NR measurements revealed that a uniform SiO₂ layer can be synthesized on an Fe layer using PHPS and that the density of the SiO₂(PHPS) layer can be altered by varying its thickness.

The density of the SiO₂(PHPS) layer was altered by varying the thickness of both the layer and the coated material whereas the conditions for forming the SiO₂ coating were not changed. Seyferth and Wiseman found that the existence of a non-cross-linked precursor results in a lower ceramic yield.²⁵⁾ In addition, Si-containing oligomers with a low molecular weight can evaporate during pyrolysis.^{26),27)} Therefore, the change in the density of the SiO₂(PHPS) layer was probably attributed to the efficiency of the cross-linking reaction between the silazane oligomers in the PHPS/*p*-xylene system. Since the surface of the Si substrate was naturally covered by a thin layer of Si–OH²⁸⁾ and because the PHPS molecules would strongly interact with the

Si–OH groups on the surface, the PHPS molecules first reacted with Si–OH group on the surface. As a result, the rate of free motion of the PHPS molecules (which correlates with the efficiency of the cross-linking reaction) in the thin layer was probably lower than that in the thick layer. In addition, the interaction between the Fe–OH groups and PHPS molecules would be stronger than that between the Si–OH groups and PHPS molecules. Specifically, the degree of interaction between the PHPS molecules and the coated material affected the density of the SiO₂(PHPS) layer (or the efficiency of the cross-linking reaction). In the case where the cross-linking reaction rate is too high, a densified SiO₂(PHPS) layer will form, and the amount of stress generated will increase, resulting in the formation of cracks. Therefore, to improve the density of the waterproof SiO₂ layer, controlling the rate of cross-linking during the curing reaction by changing the temperature or other factors is crucial.

4. Conclusions

In this study, we used the NR method to thoroughly investigate the structure of the waterproof SiO₂ layer [SiO₂(PHPS)] by using two types of substrates to model the magnetic alloy core. The analysis of the NR profiles for the model compounds showed that the SLD of the SiO₂(PHPS) layer is lower than that of natural SiO₂, and that the SLD value increases as the thickness of the SiO₂(PHPS) layer increases. The FT-IR results revealed that on unreacted PHPS material remained in the SiO₂(PHPS) layer and that SiO₄ units were formed in all samples. Therefore, we conclude that the low SLD value was mainly attributable to the formation of a low-density SiO₂ layer and that the density of the SiO₂(PHPS) layer is lower than that of natural SiO₂. The results of the NR and FT-IR analyses suggested that the observed change in the density depending on the thickness could be attributed to the efficiency of the cross-linking reaction between the silazane oligomers.

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