DEVELOPMENT OF NEW WATERPROOF THIN-LAYERS FOR THE MAGNETIC ALLOY CORE AND STRUCTURAL STUDY BY NEUTRON REFLECTOMETRY

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Abstract

The mechanism of the waterproof property of perhydropolysilazane (PHPS) and CH_3 group modified PHPS derived silica (PDS or Me-PDS) thin layers synthesized on substrates was revealed by FT-IR and neutron reflectivity(NR) analysis. FT-IR results revealed that the Me-PDS thin layer undergoes considerable C-H bond absorption. This result suggests that the synthesized thin Me-PDS layer contains large amount of methyl group The general SiO_2 network structure would be presented in the PDS and Me-PDS thin layers because both thin layers have clear Si-O absorption peaks. NR analysis revealed that the thickness of the PDS and Me-PDS thin layers was 21 nm and 22 nm, respectively. In addition, the penetration depth of water into the PDS and Me-PDS thin layers were analysed and these results suggest that the Me-PDS thin layer is more hydrophobic than the PDS thin layer, a consequence of the modification of the PDS thin layer by introduction of the hydrophobic CH_3 group.

INTRODUCTION

Silicon based ceramics such as perhydropolysilazane (PHPS) derived ceramics have been studied as coating materials to protect certain metallic components and other materials [1, 2]. PHPS and its derivatives are the useful material for the protection of metallic materials in corrosive environments. We have used the PHPS/xylene system to synthesize a PHPS derived silica (PDS) thin layers for use in the magnetic alloy core of the accelerator ring in the Japan Proton Accelerator Research Complex (J-PARC), Tokai, Japan [3]. The structure of the PDS thin layer was studied by neutron reflectivity (NR), Fourier-transform infrared spectroscopy (FT-IR), and spectroscopic ellipsometry (SE) analysis [2, 4]. As a result, detailed PDS thin layer structures and their cracking mechanism were elucidated.

In this study, we developed a new waterproof thin-layer as the magnetic alloy core protecting material using CH_3 group modified PHPS derived silica (Me-PDS). However, the structure of the Me-PDS thin layer have not yet been investigated in detail. To understand the structure of the Me-PDS thin layer and its water-proof properties, water penetration behaviour into the Me-PDS thin layer was studied using the NR analysis methods.

We prepared both thin (~20 nm) of PDS and Me-PDS layer samples to investigate the effect of the thickness on the water penetration behaviour of them. In this paper, we report the results of the NR analysis and discuss the waterproof behaviour and mechanism of these samples.

EXPERIMENTAL

Sample Preparation

The Si wafers (diameter = 5.08 cm, thickness = 0.3 mm) were supplied by SEMITEC Co., Ltd., Tokyo, Japan. The PHPS polymer was supplied by AZ Electronic Materials Co., Ltd., Tokyo, Japan. Methyltrichlorosilane was supplied by Shin-Etsu Chemical Co., Ltd., Tokyo, Japan. The Me-PHPS polymer was synthesized using the following procedures: methyltrichlorosilane and dimethyldichlorosilane were mixed in the ratio of 1:1 in toluene with bubbling of NH_3 (200 ml/min)/N_2(50 ml/min) mixed gas for 7.5 h at -60°C. The obtained toluene solution was concentrated at 200°C and the Me-PHPS polymer was obtained as high viscosity liquid. The thin PDS layer was prepared by spin coating 1.5 % of PHPS polymer/xylene solution onto Si substrates at a speed of 6000 rpm using a spin-coater (MS-A150, Mikasa Co., Ltd., Tokyo, Japan). The thin Me-PDS layer was prepared by spin coating a mixed solution, 1.5% of PHPS and 0.5 % of Me-PHPS polymers in xylene, onto Si substrates at a speed of 6000 rpm using a spin-coater. These samples were then cured at 60 °C for 1 h and allowed to stand for 48 h at room temperature. These samples were stored in pure water for 3 days at 30°C, and dried in air for 3 h before the NR experiment to remove the non-adsorbed water molecules.

FT-IR Measurement

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

The FT-IR spectra were measured with an FT/IR-4100ST (Nihon Bunko Co. Ltd., Tokyo, Japan) equipped with an ATR unit (PRO670H-S, Nihon Bunko Co. Ltd., Tokyo, Japan). The wavenumber range of the FT-IR spectra was 700 – 4000 cm^{-1} and the resolution was 4 cm^{-1}. Each spectrum was determined from the average result of 64 scans. All the measurements were performed at room temperature.

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Neutron Reflectivity Measurements

The NR measurements were performed using a BL17 SHARAKU polarized neutron reflectometer installed at the Materials and Life Science Experimental Facility (MLF) in J-PARC [4, 5]. The incident beam power of the proton accelerator was 400 kW for all the measurements. Pulsed neutron beams were generated in mercury target at 25 Hz, and the NR data were measured using the time-of-flight (TOF) technique [2, 4, 5]. The wavelength (λ) range of the incident neutron beam was tuned to approximately λ = 1.1 – 8.8 Å by a disk chopper. The incident angle was varied from 0.3° to 1.0°, and the exposure times for measurements at incident angles of 0.3° and 1.0° were 5 and 20 min, respectively. The covered Q_z range was Q_z = 0.008 – 0.109 Å^{-1}, where Q_z = $(4\pi/\lambda)\sin\theta$ (θ represents the incident angle). A 20×10 mm^2 beam footprint was maintained on the sample surface by using six different kinds of incident slits [5]. All the measurements were performed at room temperature. The data reduction, normalization, and subtraction were performed using a program installed in BL17 SHARAKU. The Motofit program [6] was used to fit the NR profiles with a least-squares approach to minimize the deviation of the fit. The thickness, scattering length density (SLD, ρ), and Gaussian roughness were also evaluated by using the Motofit program.

RESULTS AND DISCUSSION

FT-IR Analysis of the Thin PDS and Me-PDS Layer

By measuring the FT-IR spectra of the thin PDS and Me-PDS layer samples in the wavenumber range of 700−4000 cm^{-1}. The absorption of N-H (3400 cm^{-1}) and Si-H (2200 cm^{-1}), which are attributed to the unreacted PHPS [2], were not observed in the spectra. This result indicated that the starting PHPS and Me-PHPS material completely reacted in the curing process. In addition, the absorption which was observed in the region of 1100 − 1200 cm^{-1} for all sample was observed in all samples can be assigned to the stretching vibration of the Si-O bond. On the other hand, the absorption of C-H (around 2900 cm^{-1}) was observed in the thin Me-PDS layer sample. This result suggest that the synthesized Me-PDS material primarily consists of SiO$_2$ and methyl group compounds as observed from the surface measurement by the FT-IR method. Therefore, it can be considered that the thin PDS and Me-PDS layer samples form a general SiO$_2$ like network on the Si substrate.

Neutron Reflectivity Analysis

To investigate the effect of water penetration into the thin PDS and Me-PDS layer samples, the structure of the samples, which were stored in pure water for 3 days, were studied by the NR analysis method in detail.

The air-solid reflectivity measurements for the thin PDS layer samples are shown in Figure 1. The NR profiles of the samples were analysed using the Motofit reflectometry package, and the calculated theoretical reflectivity profiles are also shown in Figure 1. The circles represent the observed NR profiles, while the solid lines represent the
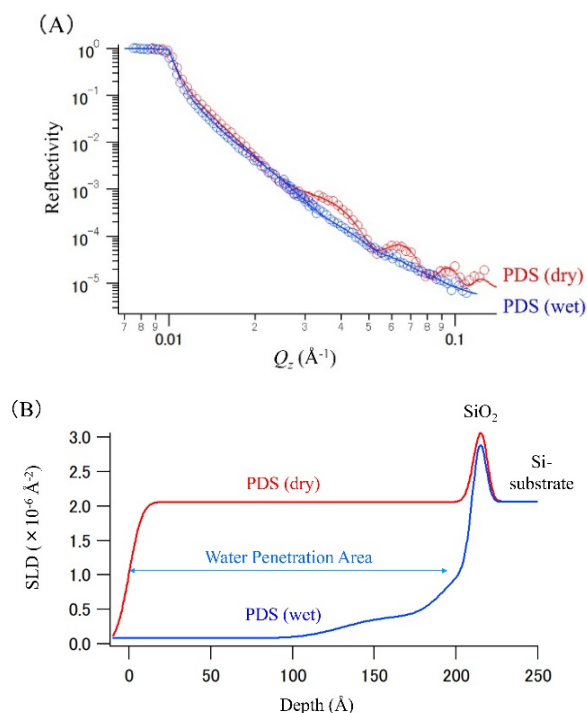

Figure 1: (A) NR profiles of the dry and wet thin PDS layer samples. The circles represent the experimental data, and the solid lines represent the best-fit calculated NR profiles. (B) Depth profiles of the dry and wet thin PDS layer samples calculated by obtained structural parameters.
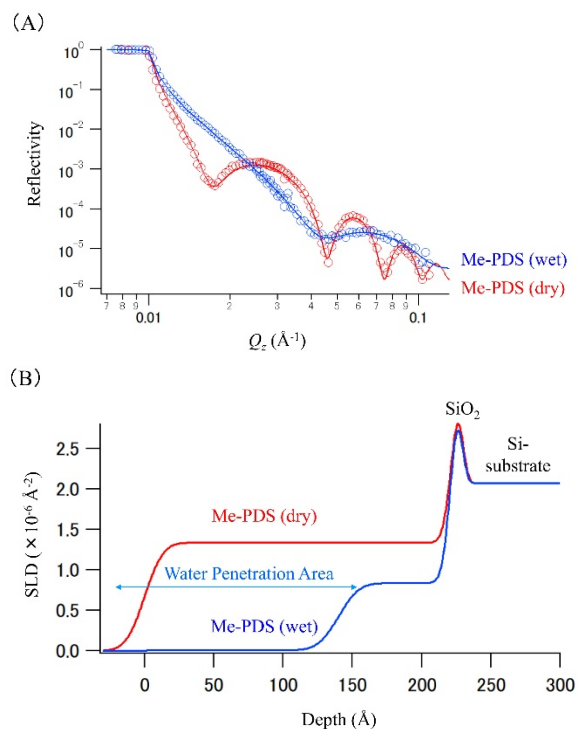

Figure 2: (A) NR profiles of the dry and wet thin Me-PDS layer samples. The circles represent the experimental data, and the solid lines represent the best-fit calculated NR profiles. (B) Depth profiles of the dry and wet thin Me-PDS layer samples calculated by obtained structural parameters.

calculated NR profiles determined from the structural models. The NR profiles of the wet thin PDS layer sample were drastically different from those of the dry sample. In addition, the peaks of Kiessig fringes become unclear. It is because the difference of the SLD between PDS layer and air becomes smaller. These changes imply that water molecules were penetrated deeper into the PDS layer. In addition, a naturally oxidized thin SiO_2 layer formed between the PDS layer and the Si substrate, a three-layer model, PDS wet /PDS dry/ SiO_2(oxidized)/Si, was applied to fit the obtained NR profiles. As shown in Figure 1(A), the theoretical reflectivity profiles reproduced the experimental NR profiles in the all Q_z-range. The thickness (t) and SLD (ρ) values of the dry thin PDS layer sample were estimated to be 211 Å and 2.06 ($\times10^{-6}$ Å^{-2}) for PDS layer and 7.5 Å and 3.47 ($\times10^{-6}$ Å^{-2}) for SiO_2(oxidized) layer, respectively. On the other hand, the t and ρ values of the wet thin PDS layer sample were estimated to be 286 Å and 0.09 ($\times10^{-6}$ Å^{-2}) for wet PDS layer, 16.3 Å and 1.21 ($\times10^{-6}$ Å^{-2}) for dry PDS layer (but still a wet), and 7.5 Å and 3.47 ($\times10^{-6}$ Å^{-2}) for SiO_2(oxidized) layer, respectively. Because lower SLD values indicate penetration of water molecules (ρ value of H_2O = -0.56 ($\times10^{-6}$ Å^{-2}) [7]) into the layers, the obtained high ρ value (0.09) clearly indicate that a large amount of H_2O is present into the PDS layer. Depth profile of the thin PDS layer samples drawn in Figure 1(B) also indicates that the water molecules were penetrated into the surface of the Si substrate.

The air-solid reflectivity measurements for the thin Me-PDS layer samples are shown in Figure 2. The NR profiles of the samples were also analysed using the Motofit reflectometry package, and the calculated theoretical reflectivity profiles are also shown in Figure 2. The NR profiles of the wet thin Me-PDS layer sample were drastically different from those of the dry sample. In addition, the period of Kiessig fringes become larger. These changes imply that water molecules were penetrated deeper into the Me-PDS layer. In addition, a naturally oxidized thin SiO_2 layer also formed between the Me-PDS layer and the Si substrate, a three-layer model, Me-PDS wet /Me-PDS dry/ SiO_2(oxidized)/Si, was applied to fit the obtained NR profiles. As shown in Figure 2(A), the theoretical reflectivity profiles reproduced the experimental NR profiles in the all Q_z-range. The t and ρ values of the dry thin Me-PDS layer sample were estimated to be 221 Å and 1.33 ($\times10^{-6}$ Å^{-2}) for Me-PDS layer and 7.4 Å and 3.47 ($\times10^{-6}$ Å^{-2}) for SiO_2(oxidized) layer, respectively. On the other hand, the t and ρ values of the wet thin Me-PDS layer sample were estimated to be 140 Å and 0.01 ($\times10^{-6}$ Å^{-2}) for wet Me-PDS layer, 81.3 Å and 0.84 ($\times10^{-6}$ Å^{-2}) for dry Me-PDS layer (but still a little wet), and 7.5 Å and 3.47 ($\times10^{-6}$ Å^{-2}) for SiO_2(oxidized) layer, respectively. Because lower SLD values indicate penetration of water molecules into the layers, the obtained high ρ value (0.01) clearly indicate that a large amount of H_2O is present into the PDS layer. Depth profile of the thin Me-PDS layer samples drawn in Figure 2(B) also indicates that a little amount of water molecules penetrated into the surface of the Si substrate. However, in contrast to the thin PDS layer sample, water penetration

into the thin Me-PDS layer sample was limited to approximately 15 nm from the surface. Since the water penetration condition is same, the difference of water penetration behaviour of the thin SiO_2 layer samples simply reflects their waterproof properties. In addition, the density of the synthesized PDS and Me-PDS could be estimated to be 1.30 and 1.01 using the obtained SLD value. Interestingly, although the density of the synthesized Me-PDS layer is lower than that of the PDS layer, the waterproof property of the Me-PDS is higher than that of PDS. Therefore, it can be concluded that the waterproof property of the thin SiO_2 layer would be improved by the modification of PHPS molecule by addition of the hydrophobic methyl group into the bulk SiO_2 network.

CONCLUSION

In this study, the structure of the SiO_2-waterproof layer, PDS and Me-PDS, was investigated in detail by the FT-IR and NR analysis methods. FT-IR analyses revealed that the general SiO_2 network structure is present both in the thin PDS and thin Me-PDS layers. FT-IR analysis also indicated that the synthesized thin Me-PDS layer primarily consists of SiO_2 and methyl group compounds as observed from the surface measurement by the FT-IR method. Additionally, NR analysis elucidated that the penetration depth of water into the thin PDS layer was deeper than that into the thin Me-PDS layer. The penetration depth of water into the thin Me-PDS layer was estimated to be 140 Å. Therefore, because under service conditions, the magnetic alloy core is covered with 1 μm of PDS waterproofing layer, it can be suggested that the modified PHPS, Me-PHPS, has a potential for utilization as an effective and thinner waterproof SiO_2 coating material.

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