

# DEVELOPMENT OF NEW WATERPROOF THIN-LAYERS FOR THE MAGNETIC ALLOY CORE: STRUCTURAL STUDIES USING NEUTRON REFLECTOMETRY

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## Abstract

Waterproof thin layers of perhydropolysilazane-derived silica (PDS), and polytetrafluoroethylene (PTFE) were synthesized on silicon substrates. The samples were studied by Fourier-transform infrared (FT-IR) spectroscopy, X-ray reflectivity (XR), and neutron reflectivity (NR) analyses. The vibrational modes of functional groups in the synthesized PDS and PTFE thin layers were determined via FT-IR spectroscopy. The density and thickness of the thin layer samples were estimated by NR and XR analyses. The obtained densities and thicknesses were 1.63 g/cm<sup>3</sup> and 30 nm for PDS, and 1.47 g/cm<sup>3</sup> and 572 nm for PTFE thin layers, respectively. Additionally, NR analysis demonstrated that the water molecules did not penetrate the PTFE layer. These results suggest that the PTFE thin layer is hydrophobic than the PDS thin layer.

## INTRODUCTION

Silicon-based ceramics such as perhydropolysilazane (PHPS)-derived silica (PDS) have been studied as coating materials to protect metallic components and materials [1]. PDS and its derivatives are useful materials for protecting metallic materials in corrosive environments [2]. The PHPS/xylene system was used to synthesize 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 using neutron reflectivity (NR) and Fourier transform infrared (FT-IR) spectroscopy [1, 2]. From the results of NR and FT-IR analyses, the structure of PDS thin-layer and their cracking mechanisms were elucidated. Further, NR analysis demonstrated that the depth of penetration of water in the PDS layers was approximately 50 nm after immersing the sample in water for 7 days [2]. This indicates that the PDS thin layer cannot be entirely protected from water impregnation.

In this study, a new waterproof thin layer of polytetrafluoroethylene (PTFE) as a magnetic alloy core protecting material was synthesized. The structure of the PTFE thin layer has not yet been investigated in detail; therefore, to discern its structure and its waterproof properties, water penetration behaviour into the PTFE thin layer was studied using the NR and X-ray reflectivity (XR) analysis methods. Herein, we report the results of the FT-IR, NR, and XR

analyses and discuss the waterproof behaviour of the PTFE thin layer.

## EXPERIMENTAL

### Sample Preparation

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. The thin PDS layer was prepared by spin coating a 1.5 % PHPS polymer/xylene solution onto Si substrates at a speed of 6000 rpm using a spin-coater (MS-A150, Mikasa Co., Ltd., Tokyo, Japan). PTFE thin layers were deposited on Si substrates via a spray coating method, which was developed by Sawahei Co., Ltd. The PTFE samples were immersed in D<sub>2</sub>O for 3 days at 20°C and subsequently dried in an N<sub>2</sub> gas box for 2 h prior to the NR experiment to remove the non-adsorbed D<sub>2</sub>O molecules.

### FT-IR Measurement

The samples for the FT-IR spectroscopy analysis were prepared by segmenting a section from each sample that was 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 Attenuated total reflectance (ATR) spectroscopic unit (PRO670H-S, Nihon Bunko Co. Ltd., Tokyo, Japan). The wavenumber range of the FT-IR spectra was 700–4000 cm<sup>-1</sup>, and the resolution was 4 cm<sup>-1</sup>. Each spectrum was determined from an average of 64 scans. All measurements were performed at room temperature.

### Neutron Reflectivity Measurements

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]. The power of the incident beam of the proton accelerator was 730 kW. Pulsed neutron beams were generated by bombarding the incident beam on a mercury target at 25 Hz, and the NR data were measured using the time-of-flight (TOF) technique [2]. The wavelength ( $\lambda$ ) of the incident neutron beam was regulated in the range of 1.1–8.8 Å by a disk chopper. The incident angle was varied from 0.2° to 1.0°, and the exposure times for measurements at incident angles of 0.2°, 0.3°, 0.6°, and 1.0° were 3, 3, 10, and 10 min, respectively. The scan was measured over the  $Q_z$  range was  $Q_z = 0.005 - 0.10 \text{ \AA}^{-1}$ , where  $Q_z =$

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$(4\pi/\lambda)\sin\theta$  ( $\theta$  represents the incident angle). A  $20\times 20$  mm<sup>2</sup> beam footprint was maintained on the sample surface using six different incident slits. All measurements were performed at room temperature. Data reduction, normalization, and subtraction were performed using a program installed in BL17 SHARAKU. The Motofit program [5] was used to fit the NR profiles using a least-squares approach to minimize the deviation of the fit. In addition, the thickness, scattering length density, and Gaussian roughness were evaluated using the Motofit program.

#### X-ray Reflectivity Measurements

XR measurements were performed using a BL8S1 reflectometer installed at the Aichi Synchrotron Radiation Center, Aichi Science & Technology Foundation, Aichi, Japan. The wavelength ( $\lambda$ ) of the incident X-ray beam was approximately 1.355 Å (9.15 keV). The incident angle was varied from 0.1° to 3.7°, and the total exposure time for the measurements was 8 min. The scan was performed covering the  $Q_z$  range of 0.10–0.30 Å<sup>-1</sup>, and all measurements were performed at room temperature. In addition, the Motofit program was used to fit the XR profiles using a least-squares approach to minimize the deviation of the fit.

## RESULTS AND DISCUSSION

#### FT-IR Analysis of the Thin PDS and PTFE Layer Samples

To determine the composition of the synthesized PDS and PTFE thin layers on the Si substrate, the molecular structures of the PDS and PTFE thin layers were analysed via FT-IR analysis.

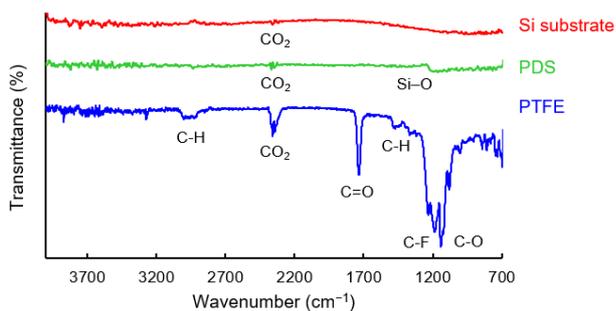


Figure 1: FT-IR ATR spectra (mean) of the PDS and PTFE thin layer samples.

Figure 1 shows the FT-IR spectra of the PDS and PTFE thin layer samples in the range of 700–4000 cm<sup>-1</sup>. The absorption observed in the region of 1100–1200 cm<sup>-1</sup> for the PDS thin layer sample is attributed to the stretching vibration of the Si–O bond. The absorption observed at 1183 and 1230 cm<sup>-1</sup> for the PTFE thin layer sample is attributed to the C–F bond of PTFE. In addition, the absorption at 1079, 1139, 1463, 1732, and 2950 cm<sup>-1</sup> for the PTFE thin layer sample is ascertained to the C–O, C–H, and C=O bonds of the acrylate polymer; the acrylate polymer was used as a binder agent for the PTFE polymer.

#### X-ray and Neutron Reflectivity Analysis

To investigate the structure of the PDS and PTFE thin layer samples in detail, nanostructure analyses were carried out using XR and NR techniques.

The air-solid NR profiles and the calculated theoretical reflectivity profiles for the PDS thin layer sample are shown in Fig. 2. The theoretical reflectivity profiles replicated the experimental NR profiles in the entire  $Q_z$ -range. The thickness and mass density of the PDS layer were estimated to be 30 nm and 1.63 g/cm<sup>3</sup>, respectively using the fitted results. Further, the results of NR analysis implied that a uniform PDS thin layer could be synthesized on the Si substrate.

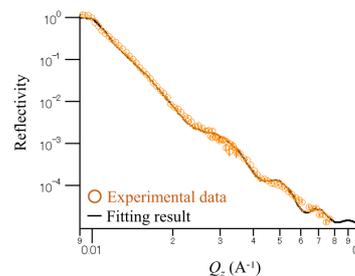


Figure 2: NR profiles of the PDS thin layer sample. The circles represent the experimental data, and the solid line represents the best-fit calculated NR profiles.

The air-solid XR and NR profiles for the PTFE thin layer sample are shown in Fig. 3. The theoretical reflectivity profiles replicated the experimental NR profiles in the entire  $Q_z$ -range. The thickness of the PTFE thin layer was estimated to be 572 nm using the Kiessig fringe period of the XR profiles. The mass density of the PTFE thin layer was estimated to be ca. 1.47 g/cm<sup>3</sup> using the fitted results of the NR data. In addition, these results suggest that a uniform PTFE thin layer was synthesized on the Si substrate. The surface roughness was estimated to be 28 nm using XR and NR analyses. The value of surface roughness indicates that the synthesized PTFE thin layer has a rough surface. The large roughness value is practical because the PTFE thin layer was synthesized via the spray coating method.

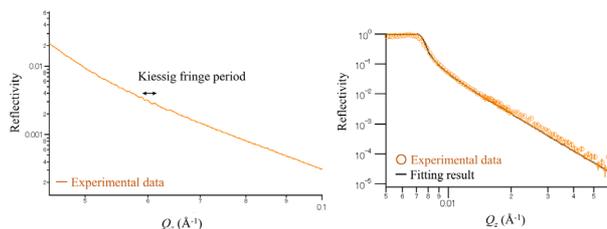


Figure 3: XR (left) and NR (right) profiles of the PTFE thin layer sample. The circles represent the experimental data, and the solid line represents the best-fit calculated XR and NR profiles.

Further, to investigate the effect of water penetration in the PTFE thin layer sample, the sample was immersed in D<sub>2</sub>O for 3 days; following immersion, the sample was stud-

ied using the NR analysis method. The air-solid NR profiles of the wet PTFE thin layer sample were the same as those of the dry PTFE thin layer sample. Based on these results, it is concluded that water molecules did not penetrate the PTFE layer. Considering the water protection ability of PDS thin layers, (depth of penetration of water in the PDS layers was 50 nm after immersing in water for 7 days) [2], the synthesized PTFE thin layer is waterproof and durable. It is concluded that the PTFE thin layer can completely resist water impregnation and protect metallic materials.

## CONCLUSION

In this study, the structure of the PDS and PTFE thin layers was investigated in detail using FT-IR, XR, and NR analysis methods. A uniform thin layer of PDS and PTFE in the direction of depth was synthesized on a Si substrate. NR analysis substantiated that the water molecules did not penetrate the PTFE thin layer. Based on these results, PTFE would be a preferable material as a waterproof thin layer to protect metallic materials in corrosive environments. However, PTFE is not a suitable material for protecting the magnetic alloy core of the accelerator ring owing to its low radiation resistance.

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