CO12-1 Thickness and Density of Adsorbed Additive Layer on Metal Surface Evaluated by Neutron Reflectometry

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INTRODUCTION: Boundary lubrication is one of the most interesting topics in the field of tribology, and the recent development of physical and chemical analyzers has created a need for better understanding of the behavior of boundary lubrication films. Under the boundary lubrication, oiliness additives mixed in base oil are expected to form adsorption layers on a sliding surface and then achieve low friction and high durability. Previous reports have confirmed that the adsorptive performance of the additive to the surface greatly affects the friction coefficient of surface. However, physical properties of adsorbed layers are still unknown because of the substantial difficulty for *in-situ* analysis.

Our laboratory has proposed applying neutron reflectometry to directly measure physical properties, i.e., thickness and density, of adsorption layers formed by acid additives on metal surfaces [1,2]. We report the physical properties of adsorption layer and introduce our latest approach with the development of the TOF-mode neutron reflectometer for tribology use.

EXPERIMENTS: To widen applications of the neutron reflectometry to tribological studies, a TOF-mode neutron reflectometer was developed at the CN-3 in Kyoto University Research Reactor Institute (KURRI). A schematic diagram is shown in Figure 1. The carbonization nickel surfaces with various film thicknesses were deposited on ultra-flat silicon blocks by physical deposition. The obtained reflectivity profiles in air proved that the resolution of the developed reflectometer for film thickness was under 2 nm. This result proved that the reflectometry has high potential for use in advanced tribological studies on solid-liquid interfaces.

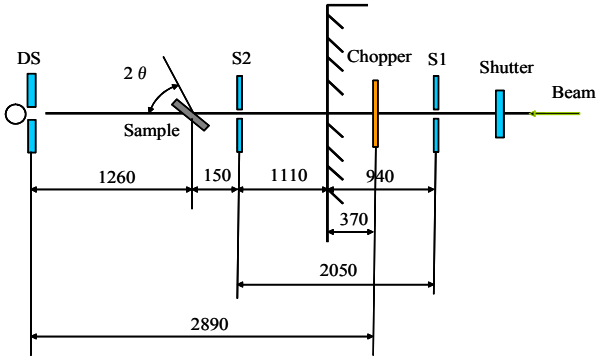

Fig. 1. Schematic diagram of reflectometer in KURRI.

RESULTS: The carboxylic groups in the acetic acid in the lubricant were expected to preferentially adsorb to the metal surface and form a thin layer less than 10 nm thick. To examine the layer thickness and density using neutron reflectometry with the highest accuracy, we took the following procedure. First, we set the sample surface in the sample holder to obtain a neutron reflectivity profile from the interface between the sample surface and air. Second, the base oil poly-alpha-olefin (PAO) was poured into the sample holder and a reflectivity profile from between the surface and the PAO was similarly obtained. Finally, the additive was added into the PAO and mixed in the sample holder carefully and the reflectivity profile was again obtained. During the whole experiments, we didn't touch the neutron optics and the sample holder at all, and thus the difference in reflectivity profiles in each step were completely recognized as being provided by the existence of base oil and/or additive at the interface. After the above procedure, we checked the difference between the reflectivity profiles with theoretical fitting based on Parratt's theory. The amount of additive mixed into PAO was 0.1 mass%.

The obtained reflectivity profile is shown in Fig. 2. From the obtained reflectivity profiles, the thicknesses of the adsorption layer on the copper surface were quite thin, approximately 1.0-2.5 nm. To investigate the effect of adsorption layer on the tribological properties, friction tests were carried out for copper surfaces with a ball-on-disk tribometer. The results showed that the friction coefficient decreased when any additive was mixed into the base oil. The results are summarized as follows.
(1) Formation of the adsorption layer was clearly observed when the acetic, undecanoic, and stearic acids were used as additives for each. Particularly, the adsorbed layer of acetic acid was expected to be a multi-layer one.
(2) Oiliness additives with long carbon-chains required several hours to form the stable adsorbed layers.

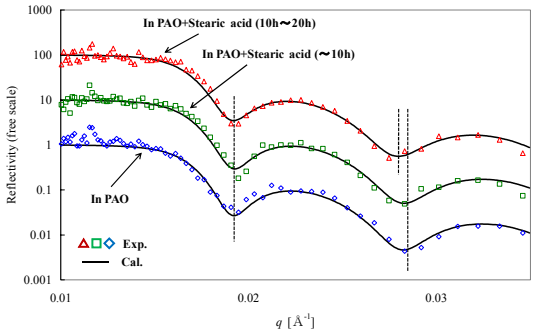

Fig. 2. Reflectivity profiles from copper surface.

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採択課題番号 23014　中性子反射率法による金属表面上添加剤吸着層の厚み・密度測定　共同通常（同志社・理工）平山朋子、小西洋平、前田成志、松岡 敬（京大・原子炉）日野正裕、北口雅暁、小田達郎

CO12-2 **Neutron Activation Analysis on Hafnium Oxide Films**

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INTRODUCTION: Hafnium oxide (high-k) dielectric films are being introduced into silicon-based semiconductor devices in order to achieve higher electronic performance. The front-end processes require the thin dielectric films well-controlled in thickness for gate stacks. According to the international technology roadmap for semiconductors 2011[1], thickness of dielectric films should be controlled in 4 % process range. It becomes difficult to obtain the accurate thickness in length unit since the films are getting to be near atomic dimension and consist of complex structure like interface layers, which may involve atomic fluctuations. Reference materials whose properties are well-calibrated should shed light on quantification of the film thickness with small uncertainties. This study aims to quantify hafnium in thin hafnium oxide films by isotope dilution neutron activation analysis [2] as quantitative method, and finally to develop reference materials applicable to semiconductor manufacture.

EXPERIMENTS: Hafnium oxide films were deposited on 4-inch Si wafers by magnetron sputtering method. In this study, the targeted thickness is 2.5 nm with homogeneity within 1% in a wafer. Several wafers with hafnium oxide film were diced into 15 × 15 mm^2 pieces, and several pieces were randomly picked-up for measurements.

Hafnium amounts were evaluated by INAA and calculated into area density. The surface area of a specimen was measured by taking images using a commercial optical scanner with a high resolution. From the images, the lengths of four sides of the chip were measured to calculate the surface area. Length calibration was performed by standard scales. For the production of standards to calibrate hafnium amounts, a natural standard solution was prepared by diluting SRM 3122 (commercially available from NIST) gravimetrically. In addition, a spike solution for isotope dilution was prepared by dissolving a ^{179}Hf enriched HfO_2 in HNO_3+HF+H_2SO_4 solution, followed by diluting gravimetrically. Portions of the solutions were dropped from a polyethylene pipette onto pieces of the cleaned specimen and blank Si chips. All specimens and standards were heat-sealed in individual clean poly-ethylene envelopes and stacked in a poly-ethylene irradiation container. The neutron irradiation was performed for 4 hours at 1 MW in research reactor KUR of Research Reactor Institute, Kyoto University. Gamma-ray activity of each specimen and standard was measured by a high-purity germanium detector (ORTEC) with an energy resolution around 1.8 keV FWHM at 1333 keV.

RESULTS: Figure 1 shows a gamma ray spectrum obtained from the specimen of spike solution on hafnium oxide film. Several peaks can be clearly seen and some of them are from ^{181}Hf and ^{180m}Hf as indicated in Fig.1. The peaks at around 133 keV and 215 keV were picked up, the counts in each peak were integrated for every specimen and standard, and then the intensities after the decay correction [3] were used to determine hafnium amount in the oxide film. The hafnium content in the specimen is estimated to be 4.3 μg, calculated by using the formula shown in Ref [2]. Considering the surface area of the hafnium oxide film is 223 mm^2, the resulting hafnium content is in agreement with the content estimated from the film thickness.

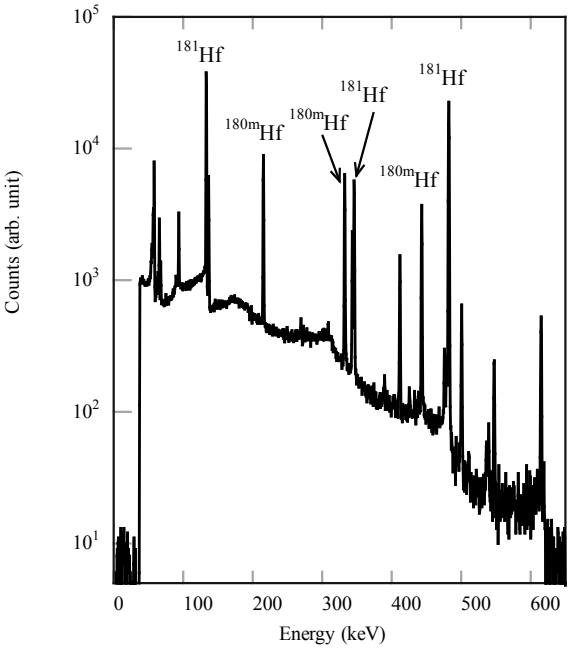

Fig. 1. Gamma ray spectrum of the spike solution on hafnium oxide film.

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採択課題番号 23071 中性子放射化分析によるハフニウム酸化膜中ハフニウムの定量　　一般通常
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CO12-3 **A Brain Radiation Necrosis Model in Laboratory Animals**

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INTRODUCTION: Since medical treatment apparatus progressed in recent years, the high dose radiotherapy to the brain tumor becomes possible, and, as a result, the prognosis of the brain tumor has improved. On the other hand, the brain radiation necrosis which arises during the long-term observation period after intensive radiotherapy becomes a serious problem. Although a part of molecular mechanism in a brain radiation necrosis was shown by our previous research, in order to prove these hypotheses strictly, it is necessary to create a brain radiation necrosis model in laboratory animals, and to analyze the pathology for each stage. Understanding the regulation mechanism of the cytokine in the brain radiation necrosis may have an important role in the treatment development.

EXPERIMENTS: Fifty 12-wk-old female Sprague-Dawley rats with body weight 229 ± 20 grams were divided into 5 separate batches to receive irradiation of 20, 25, 30, 35 or 40 Gy to the right hemibrain with a single collimated (10mm × 10mm) ^{60}Co gamma-ray irradiator under anesthesia. Gamma-ray irradiation was applied using a ^{60}Co gamma-ray irradiator in the KUR. The irradiation method referred to the report of Wang et al., Li et al., and Nordal et al.[1, 2, 3]. Three rats died due to anesthesia. A total of 47 rats were irradiated with 20 Gy (n = 5), 25 Gy (n = 5), 30 Gy (n = 22), 35 Gy (n = 10) and 40 Gy (n = 5), respectively.

RESULTS: In all rats in the 40 Gy cohort, body weight decreased and died within several days after irradiation. Seven rats in the 35 Gy cohort and ten rats in the 30 Gy cohort were found to have abnormal signs of gait and movement from 24 weeks post-radiation. No gross neurologic abnormalities were observed in other rats. Standardized H&E staining was used to detect morphologic characteristics of brain tissue between 20 and 28 weeks after irradiation. There were no apparent histopathological abnormalities in the brain, including white matter and blood vessel changes after all dose, as shown in Fig.1.

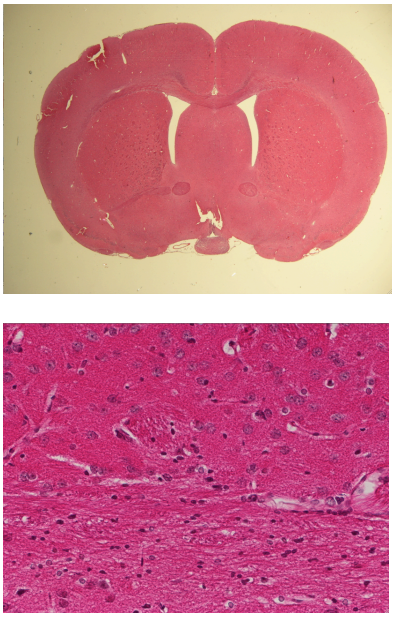

Fig. 1.
H&E staining in the specimen of the 35 Gy irradiated brain 20 weeks after irradiation. There were no apparent histopathological abnormalities. (Original magnifications, ×10, ×200)

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採択課題番号 23072　　放射線壊死の病態解明と新規治療法の研究　　共同通常
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（京大・原子炉）小野公二、増永慎一郎、田中浩基、近藤夏子

CO12-4 Characterization for U-type and Straight-type ^{3}He PSD

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INTRODUCTION: Development of neutron detectors is a key to realize new instruments in Materials and Life Science Experimental Facility in J-PARC. Although various detectors have been developed, position sensitive detectors (PSD) with ^{3}He gas still have superior to the others in counting rate and so on. For DNA back scattering instrument installed at the BL02 port [1, 2], U-type PSD which consists of two short straight PSD's connected at the one end have been newly developed as counters for inelastic experiments (see Fig. 1) as well as a conventional straight-type PSD for diffraction. Hardness to obtain ^{3}He gas is a serious problem in neutron science. Therefore, we need to optimize diameter and gas pressure of PSD. The purpose of this study is to measure positional resolutions for various ^{3}He PSD's with different gas pressures and shapes and to obtain direction in detector optimization. Moreover, newly developed U-type detectors for DNA must be examined for quality stabilization respective in positional resolution.

EXPERIMENTS: The PSD detectors, an amplifier and a power source for PSD were supplied by Toshiba Electron Tubes & Devices Co., Ltd. To investigate positional resolution, proportionality and detectable region of PSD, CN-2 port was utilized during Oct. 4-6 and Nov. 15-16, 2011. Neutron beam irradiated a PSD set on the sample table through a slit of 1mm in width and 14mm in height. 5 minute irradiation at the reactor operation of 1MW provides enough counts around 2.4×10^4 at the peak for PSD with 6 atm ^{3}He gas and 1/2 inch diameter.

RESULTS: Fig. 1 shows the sketch of the U-type ^{3}He PSD and the irradiated position. Fig. 2 shows the results for the positional resolutions of (a) the U-type PSD with 6 atm ^{3}He gas in the tube of 1/2 inch diameter and (b) the straight PSD with 1/2 inch diameter and 6 atm ^{3}He gas pressure. In general, the positional resolution of PSD is higher at the middle of the tube than at the end. Even U-type PSD exhibits such a tendency. Both the open edges of U-shape show larger FWHM values, while the connected bottom of U-shape shows a relatively small FWHM. The proportionality of the detecting position is quite good for both U-type and straight-type PSD's. A 300 mm length straight PSD with 21.4 atm gas pressure in the 1/4 inch tube has the highest resolution of 3.43 mm due to the effects of gas pressure of ^{3}He, small diameter of the tube.

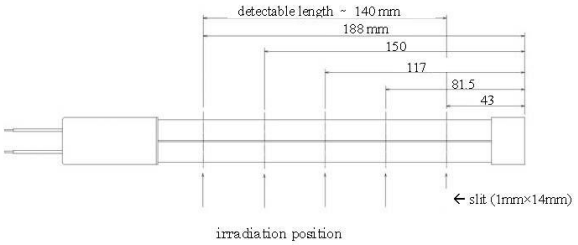

Fig. 1. Sketch of U-type ^{3}He PSD and the irradiated positions .

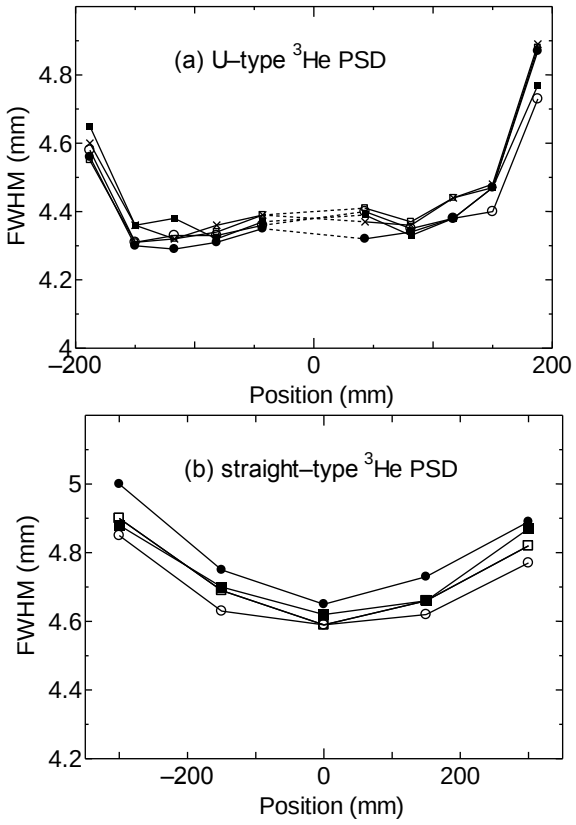

Fig. 2. Positional resolution of (a) U-type ^{3}He PSD at the positions of ±43, ±81.5, ±117, ±150, ±188 mm from the connection (the bottom of the U shape) and (b) straight-type ^{3}He PSD at the positions of ±300, ±150, 0 mm (center of the tube).

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採択課題番号 23079 U 字型および直管型 3He 位置敏感型中性子検出器の性能評価　共同通常
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（総合科学研究機構）柴田薫、蒲沢和也、山田武（京大・原子炉）杉山正明

CO12-5 Evaluation for Radioactive Inventory of Structural Materials Induced by Neutron Activation

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INTRODUCTION: In decommissioning of nuclear power plants, radioactive inventory of structural materials in the facility induced by neutron activation generated from the reactor is a major problem. For example, in view of estimation for exposure of occupationally exposed persons involved in demolition work of nuclear facilities, public safety assessments, plans for demolition work of nuclear facilities, evaluation of radioactive wastes, and so on. Evaluation for radioactive inventory is necessary information to carry out decommissioning safely and reasonably.

Evaluation for radioactive inventory, however, becomes overly conservative by being taken likelihood on the safety assessment in the present situation. As problems in the evaluation, there are three points as follows.

- Accurate material composition should be used for domestic nuclear facilities.
- Newest activation cross section should be used in the evaluation.
- Realistic spectrum should be used on the assumption of neutron energy spectrum of a typical LWR.

This study focuses on material composition, and calculate radioactive inventory more reasonable. The purpose of this study is to contribute to improve the accuracy of the evaluation of radioactive inventory, focusing particularly on the main structural materials [1], [2], [3].

EXPERIMENTS: This experiment aims to establish an experimental system that simulates the neutron spectrum of a typical LWR. Optimal moderator to reproduce the neutron spectrum of a typical LWR is evaluated by Using MCNP-5. And then, the neutron irradiation experiment is implemented through an evaluated moderator.

In order to reproduce the spectrum of typical LWR, it is necessary to moderate the energy spectrum of neutrons of Slant. As a moderator, 250μm thickness cadmium is adopted for the adjustment of the spectrum. According to Figure 1, moderated spectrum is close to the goal spectrum of LWR.

In this experiment, irradiated materials are Iron and SUS304. Size of the Iron sample is 10mm diameter and 20mm height, and weight is about 12g. And size of the SUS304 sample is 1.0mm diameter and 20mm height, and weight is about 0.12g. These samples should be put in polyethylene capsule.

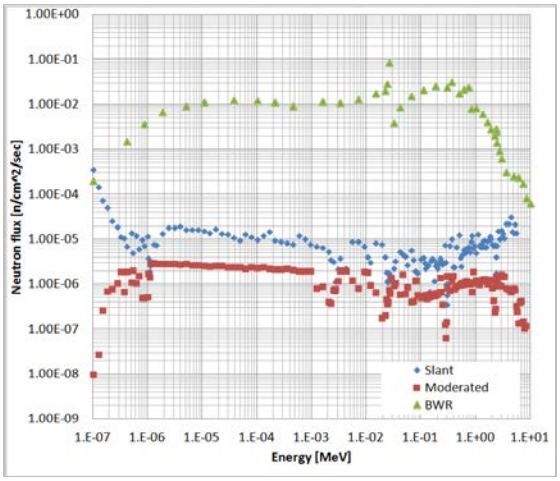

Fig.1 Transmission spectrum

RESULTS: Table.1 shows a list of radioactivity of each nuclide in irradiated Iron. Radioactivity of Mn-56 is seen remarkably. But radioactivity of other nuclides is not seen well. Table.2 shows a list of radioactivity of each nuclide in irradiated SUS304. Radioactivity of Mn-56 is also seen remarkably. And radioactivity of ^{51}Cr and ^{58}Co are seen

Table.1 List of radioactivity (Iron)

γ energy [keV]	Nuclide	Net	cps	Half life [sec]	Emission rate	Radioactivity [Bq]	Radioactivity per mass [Bq/g]
511	γ±	12311	0.5				
850.8	Mn-56	293766	2277.3	9284.4	0.989	324063	27275
1099.2	Fe-59	743	5.8	3844800	0.565	1192	100
1810.6	Mn-56	49368	382.7	9284.4	0.272	359982	30299

Table.2 List of radioactivity (SUS304l)

γ energy [keV]	Nuclide	Net	cps	Half life [sec]	Emission rate	Radioactivity [Bq]	Radioactivity per mass [Bq/g]
320.1	Cr-51	4197	0.17	2393280	0.0983	78	617
511	γ±	12311	0.50				
810.8	Co-58	1309	0.05	6117120	0.994	5	39
846.8	Mn-56	7325	0.29	9284.4	0.989	15455	122276
1810.6	Mn-56	1152	0.05	9284.4	0.272	16099	127366

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採択課題番号 23082 放射性核種生成量評価のための中性子による材料照射の研究 共同通常
（京大・原子炉）高宮幸一（東大院・工）新谷俊幸、 熊谷一城、 小佐古敏荘