VIII-Ⅱ-1.　Project Research

Project 9

PR9 Project Research on Development of Scattering Spectrometers Utilizing Small and Medium Class Neutron Source

M. Sugiyama

Research Reactor Institute, Kyoto University

Objectives and Allotted Research Subjects: Recently, J-PARC has started to supply very intensive pulse neutron beam. This means that research with neutron is getting into new world. However, only with J-PARC, we cannot to sustain this new research world. Especially, it is inevitable to check new idea, to analyze industrial products and to educate new comers. For this purpose, we think small-and/or medium class neutron sources are very suitable. As a corollary, beam intensity from these size neutron sources is not so strong. Therefore, we face what can we do and/or how can we do effective research with these neutron source. In order to answer these questions, we have started this research project with the following six allotted research subjects.

ARS-1: Nano-Scale Structure Measurements of Micelles by Utilizing KUR-SANS. (K. Hara, T. Yanagino, T. Miyazaki, S. Yoshioka, Y. Oba, N. Sato1 and M. Sugiyama)

ARS-2: Evaluation of high-q data of KUR-SANS for quantitative analysis of precipitates in steels. (M. Ohnuma, Y. Oba, P.Kozikowsky and M. Sugiyama)

ARS-3: Development of Small-Angle Scattering Calculation Code (M.Sugiyama, and Y.Ueki)

ARS-4: Development of compact SANS monochromator for steel-related sample use of KUR-SANS (M. Hino, Y. Oba, T.Oda, M. Sugiyama)

ARS-5: Dvelopment of sample cell for in-situ SANS experiments using hydrogen absorbing materials. (K. Mori, K. Iwase, Y. Oba, T. Ichida, T. Fukunaga, and M. Sugiyama)

ARS-6: Small-angle Neutron Scattering Analysis of Radiation-Fabricated Thermoresponsive Binary Hydrogels. (N. Sato, Y. Oba, M. Sugiyama)

Main Results and Contents of This Project:

ARS-1: Hara et.al. investigated nano-scale structures of micelles with KUR-SANS. With sodium oleate solution, they obatined very clear SANS profile with KUR-SANS and confirm that the revealed structure well agrees with that obtained by SAXS. This result indicates that KUR-SANS (installed at medium class neutron source) is also useful to this research filed.

ARS-2: Ohnuma et.al. evaluated KUR-SANS data of steel. which is one of main targets of KUR-SANS, with SANs data obtained with the other intensive neutron spectrometers. There are some discrepancy in high q-region. The reason is discussed in the report.

ARS-3: Sugiyama and Ueki are developing the data analysis program. They developed the SANS simulation of protein and also special cage. Their simulation well reproduces the experimental results.

ARS-4: Hino et.al. developed a new monochromator for KUR-SANS. The monochromator supplies 4.8Å neutron suitable for structural investigation of steel.

ARS-5: Mori et.al. developed sample cell for in-situ SANS experiments using hydrogen absorbing materials In situ experiment is inevitable to understand hydrogen behavior and distribution in the storage material.

ARS-6: Sato et.al. studied γ-radiation-fabricated thermo-responsive binary hydrogels. The structure and character of this new material have not been clarified so much. Sato revealed the structure with KUR-SANS.

採択課題番号 24P9 中小型中性子源を用いた散乱分光システムの開発 プロジェクト
（京大・原子炉）杉山正明

PR9-1 Nano-Scale Structure Measurements of Micelles by Utilizing KUR-SANS

K. Hara, T. Yanagino, T. Miyazaki, S. Yoshioka, Y. Oba[1], N. Sato[1] and M. Sugiyama[1]

Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University
[1]*Division of Quantum Beam Material Science, Research Reactor Institute, Kyoto University*

INTRODUCTION: The authors have been investigating the nano-structures of the hydrocolloids, such as hydrogels and surfactants, which are composed of dispersoid and water. By the alteration of the interactions between the ingredients, they often show drastic changes in the nano-scale structures. In the present investigation, the authors have examined the performance characteristics of the KUR-SANS system installed at Research Reactor Institute, Kyoto University by investigating such a nano-scale structure of a surfactant, sodium oleate (SO), in heavy water. By the present examination, the KUR-SANS system has demonstrated a competent performance to get the SANS profiles of such a surfactant.

EXPERIMENTS: The SANS experiments were performed with the KUR-SANS system installed at Kyoto University Reactor, Kumatori, Japan. 30 mM sodium oleate (SO) heavy-water solutions were prepared and were sealed into quartz cells. The small angel neutron scattering (SANS) profiles were observed for the 30mM SO D_2O solutions after having been left intact for 24 hours at room temperature. Figure 1 shows the 2-dimentsional distribution of the scattered neutron intensity scattered from the SO solution observed by the KUR-SANS system. Figure 2 shows the SANS profile derived by integrating the 2D intensity distribution in the same circumference. Figure 3 is the small angel X-ray scattering (SAXS) profile of the SO solution observed with an SAXES optics installed at BL-10C of the Photon Factory in High Energy Accelerator Research Organization (KEK), Tsukuba, Japan for the comparison with the SANS profile.

RESULTS: The SANS profiles obtained with the KUR-SANS system are in good quality as shown in Fig. 2, which are the typical ones observed in many micelles, indicating a competent performance of the system. The micellar structure in the SO could be confirmed by the SAXS profiles observed with the SAXES system, which are also observed in many micellar structures of surfactants.

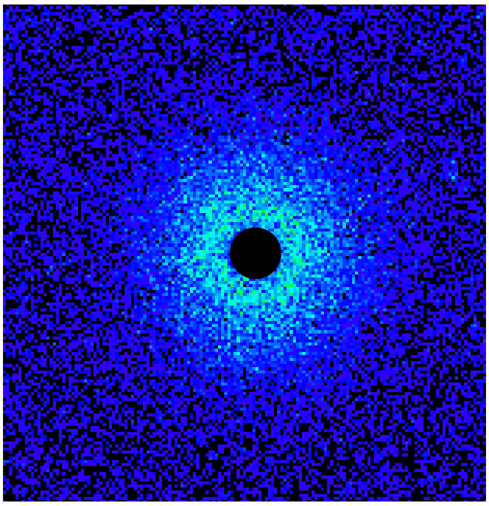

Fig. 1 2D Intensity Distribution of Scattered Neutron from 30mM Sodium Oleate in D_2O observed by KUR－SANS

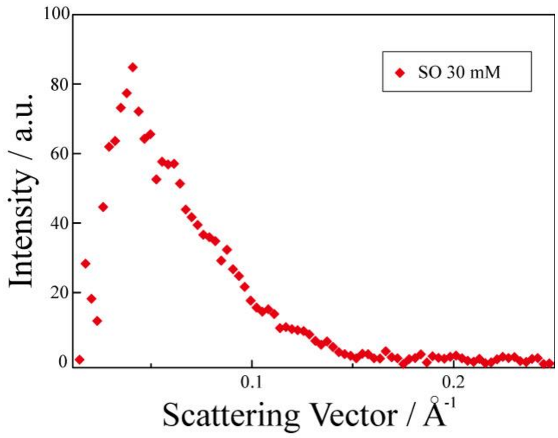

Fig. 2 A SANS Profile 30mM Sodium Oleate in D_2O observed by the KUR-SANS system.

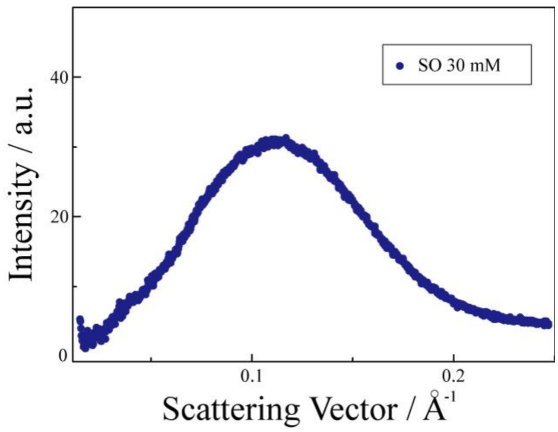

Fig. 3 A SAXS Profile 30mM Sodium Oleate in D_2O observed by the SAXES system.

採択課題番号 24P9-1　KUR-SANS を用いたハイドロコロイド分散系の中性子小角散乱観測　プロジェクト
（九大院工）原　一広、柳野 智、宮崎智博、吉岡 聰
（京大原子炉）大場洋次郎、佐藤信浩、杉山正明

PR9-2 Evaluation of High-q Data of KUR-SANS for Quantitative Analysis of Precipitates in Steels

M. Ohnuma[1], Y. Oba[2], P.Kozikowsky[1,3] and M. Sugiyama[2]

[1]*National Institute for Materials Science*
[2]*Research Reactor Institute, Kyoto University*
[3]*Warsaw University of Technology*

INTRODUCTION: Due to the high demands of SANS in the field of materials science, the role of SANS installed in the medium scale or compact type neutron source becomes important. The performance of SANS instruments installed in compact source can never overcome the one in large-scale facilities, however, it can give enough information in the focused q-range corresponding the target scale in real space. Our target q-range for SANS in compact source is the range from 0.1 to 3 that corresponds to the range covered by laboratory SAXS. Once the q-range is cover by SANS in KUR, it bring much broader applications using the way for the compositional analysis based on the contrast difference between SANS and SAXS(1-3). For this purpose, we have measured same samples using different SANS instruments together with KUR-SANS.

EXPERIMENTS: The steels for tools, class SCM450 (0.4wt%C) was used for the comparison among the three different facilities, i.e. TAIKAN in J-PARC, HANARO-18m SANS (Korea) and KUR-SANS. For separating magnetic and nuclear component, different magnet was used depends on the facilities. The field for 0.5 1.0 and 0.6T is used for TAIKAN, 18m SANS and KUR-SANS, respectively. Because all the fields are larger than the saturation field of pure iron, the fields are assumed to be enough for saturating the measured sample. Measurements have been performed using the monochromator for the wavelength of 0.47nm.

RESULTS: Figure 1 shows a SANS profile of SCM450 tempered at 550ºC. The profile measured in HANARO is in absolute scale and the others are shifted for overlapping profiles parallel to the magnetic field. Data measured in KUR-SANS are shown in markers (circles(red) : parallel to the field (nuclear component), squares(blue) : perpendicular to the field (sum of magnetic and nuclear component)). Compare to the profiles obtained in 2011 in KUR-SANS, the statistic has been modified drastically by the newly developed monochromator. Nevertheless, there are the discrepancy between profiles obtained by KUR-SANS and TAIKAN (blue and red solid curves), especially in high-q region. Judging from the same level of both blue squares and red circles, it must attribute to a relatively high level of constant background. The levels of the profiles measured perpendicular to the field are basically same between those measured in KUR and TAIKAN. However, the level measured in HANARO is higher than others. This result suggests that the SANS intensity may still depend on the field suggesting that the field of 0.6T is still smaller than the saturation field. It will be discussed by magnetic measurements and/or the comparison of SANS profiles in absolute unit.

In conclusion, the statistic of the KUR-SANS profiles have been drastically modified and almost reached for regular use. However, there are still some spaces for discussion, like possibility for making background lower and validity of the applied field level.

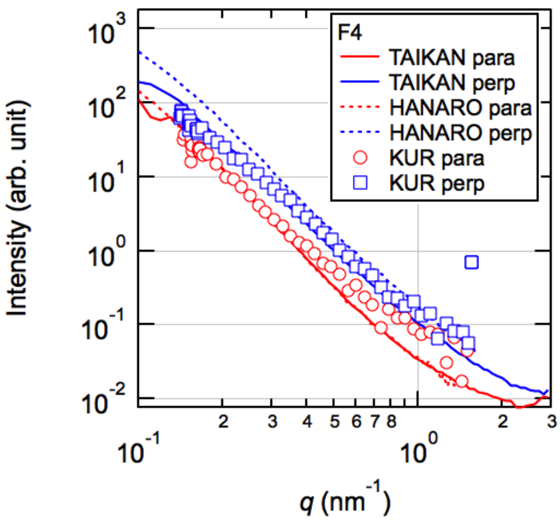

Fig.1 SANS profiles of SCM450 tempered at 550ºC measured using different SANS. markers: KUR-SANS, solid curves: TAIKAN and dotted curved HANARO. colors indicates the direction of scattering vectors, blue: perpendicular to the magnetic field, red: parallel to the magnetic field

採択課題番号 24P9-2　　高 q 領域の SANS と SAXS を併用した鉄鋼中ナノ析出物の定量評価法　　プロジェクト
（物材機構）大沼正人, Pawel Kozikowsky, （京大原子炉）大場洋次郎, 杉山正明

Development of Small-Angle Scattering Calculation Code

M. Sugiyama and Y. Ueki

Research Reactor Institute, Kyoto University

INTRODUCTION: Small-angle scattering is a very powerful tool to analyze the particle structure in solution. This technique gives us the roughly estimation of size and shape of the particle. However, it is difficult to reveal the detailed structure from scattering profile. In these days, we are developing several calculation and simulation codes to overcome this problem. As a result, SAS calculation program for protein has been almost completed: the program calculates SAS profile (SAXS and SANS) from PDB data considering surrounding water. So, as a next step, we are trying to apply this program to analyze to another kind of particle, organic cage which was developed by Fujita group in University of Tokyo and a promising material for use of drug delivery and so on. Here, we report the result of analysis of status of cage material in solution.

EXPERIMENTS: The structure of Cage particle is shown in Fig 1.

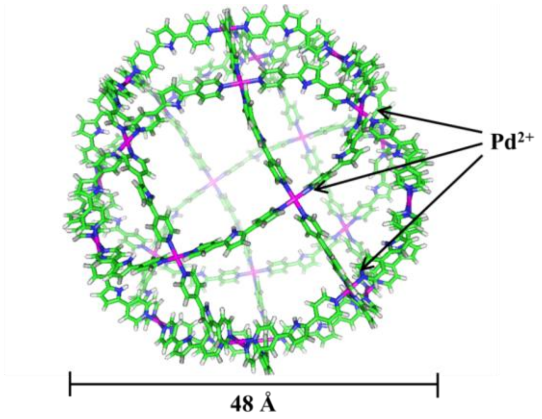

Fig. 1. Structure of Cage material. Cage composed with five-membered ring connecting by Pd.

The SAXS experiments were carried out at room temperature with a SAXS apparatus installed at BL45XU of SPring8, Hyogo, Japan. (Measurement time is 10sec with concentration of 1mg/ml)

RESULTS: Figure 2 shows SAXS profiles of Cage material. We also calculated SAXS profile with atomic coordinates of Cage material by our SAS program. However, the calculated SAXS profile does not reproduce the observed one. Here, we consider the aggregation of the Cage material. The Solid line in Fig.3 shows the calculated SAS profile with the ratio of monomer and dimer of 1:0.13. As you can see, the calculated profile well reproduce the experimental one except for the profile in the higher *q*-region>0.3Å^{-1}. Therefore, we consider the remaining chemicals after the formation reaction. The candidates of remaining chemicals were Pd(OTf)$_2$ and Ag(OTf) and we re-calculated SAXS profile taking consideration of scattering from the remaining chemicals: they are small molecules which increase the intensity in the higher q-region. The re-calculated SAXS profile well reproduce the experimental one.(Fig.4.)

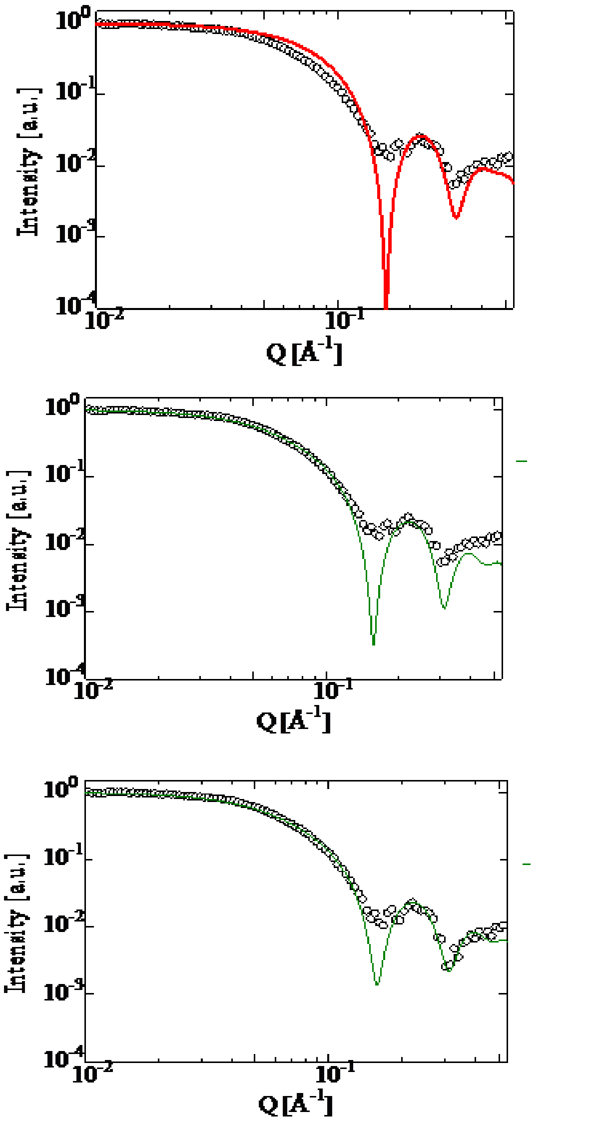

Fig. 2 Observed SANS profile and simulated ones.

PR9-4 Development of Compact SANS Monochromator for Steel-Related Sample Use of KUR-SANS

M. Hino, Y. Oba, T. Oda[1], M. Sugiyama

[1]*Research Reactor Institute, Kyoto University*
[2]*Department of Nucl. Eng., Kyoto University*

INTRODUCTION: Small angle neutron scattering (SANS) technique is very powerful to investigate of structure of complex material with size of 1-100 nm. The scope of application is very wide and there are a lot of interesting sample with strong scattering intensity. A lot of researchers are interested in steel-related sample and the scattering intensity is strong. Thus KUR-SANS [1] with 1MW reactor operation is still very useful and important to improve the instrument. There are two monochromators in which average wavelength is 0.28 and 0.55 nm in the KUR-SANS [1,2]. The monochromators are double reflection type as shown in Fig.1 and they don't change reflection angle depend on wavelength. The d-spacings of these monochromators for 0.28 and 0.55 nm are 7 and 14 nm, respectively. The acceptable beam width of 8 mm is not large. Currently, the monochromator for 0.55 nm is not so effective since Cold Neutron Source (CNS) at KURRI does not operate. These monochometers are not optimum for steel-related sample since the required wavelength is longer than 0.42 nm to avoid Bragg diffraction from the crystal part of the steel-related sample. The optimum average wavelength is about 0.47 nm in which wavelength resolution of 20% in FWHM. The d-spacing of required multilayer was 11.8 nm since the incident angle is 20 mrad. In this study, we show the performance of new monochromator for steel-related sample at KUR-SANS.

EXPERIMENTS: The multilayer mirrors deposited on both surface of silicon substrates in which size of 64x32x0.6 mm. They were fabricated by using ion beam sputtering machine at KURRI. The reflectivity measurement was carried out at CN-3 beam line.

RESULTS: Figure 2(a) shows comparison between direct beam and reflected beam by new monochromator with collimated beam condition. The slit width and divergent angle were 5 mm and 2.7 mrad, respectively. The reflected beam well extracted from direct beam. The wavelength of maximum intensity was estimated to be 0.48 nm and the resolution is 16 % in FWHM. In Fig.2(b), the background level, in particular effect of $\lambda/2$ reflection, was dramatically reduced by using double reflection configuration.

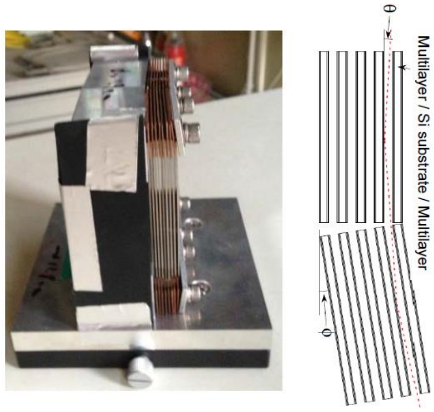

Fig.1 The photograph of monochromator and layout of the two set of NiC/Ti multilayer mirrors for KUR-SANS. Here ϕ is equal to 2θ.

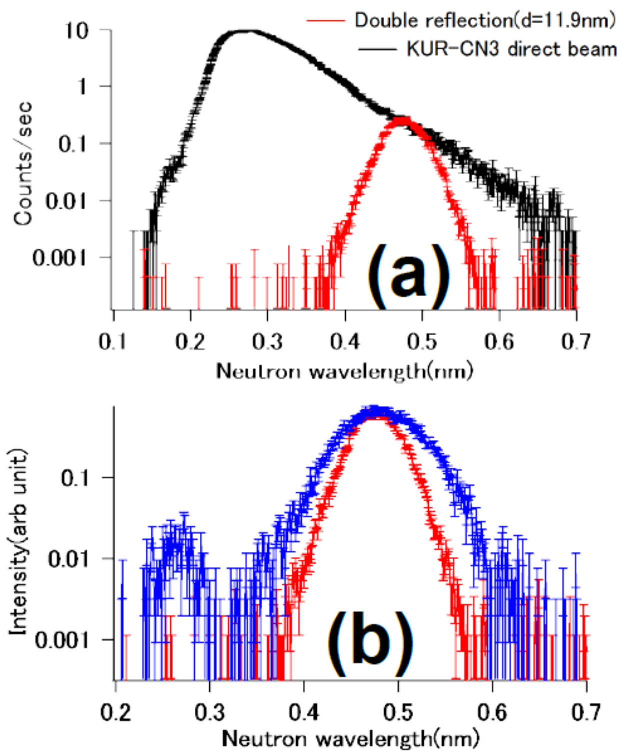

Fig.2 in comparison of (a) Direct beam and measured reflectivity of the monochromator, (b) reflectivities of single and double reflection in the monochromator, respectively.

REFERENCES:

[1] M.Sugiyama, *et al.*, JJAP, 33(1994) 6396.
[2] H.Sunohara, M.Hino, et al.,Physica B, 350(2004) 869.

採択課題番号 24P9-4 2次元集光デバイスと(偏極)小角散乱用小型モノクロメーターの開発 プロジェクト

（京大・原子炉）日野正裕、杉山正明、北口雅暁（京大・工）小田達郎、田崎誠司

PR9-5 Dvelopment of Sample Cell for In-situ SANS Experiments Using Hydrogen Absorbing Materials

K. Mori, K. Iwase[1], Y. Oba, T. Ichida[2], T. Fukunaga and M. Sugiyama

Research Reactor Institute, Kyoto University (KURRI)
[1]Department of Materials and Engineering, Ibaraki University
[2]Graduate School of Engineering, Kyoto University

INTRODUCTION: It is well known that Ti-Cr-V alloys are excellent hydrogen absorbing materials, together with intermetallic compounds such as $LaNi_5$ and Mg_2Ni. The Ti-Cr-V alloys exhibit an enormous maximum hydrogen storage capacity (i.e., with a H/M value of 2, where H/M is the hydrogen-to-metal ratio); therefore, these materials have attracted much attention as promising candidates for hydrogen storage applications such as high-pressure metal hydride tanks in fuel-cell vehicles.

To characterize the hydrogenation properties by assessing the state of the surface of the powder particles in the Ti-Cr-V alloy is very important. Although a variety of investigations on the microstructure and morphology of the Ti-Cr-V alloys by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have been conducted in previously reported studies [1], sufficient information on the surfaces of particles in Ti-Cr-V alloys subjected to hydrogenation is deficient. On the other hand, small-angle neutron scattering (SANS) is widely recognized as a powerful tool for observing the particle-surfaces of industrial materials [2]. We expect that SANS can serve as an appropriate technique to obtain information on the particle-surfaces in the case of Ti-Cr-V alloys as well.

In this work, we developed a sample cell for in-situ SANS experiments (in-situ cell) with the SANS spectrometer of Kyoto University Research Reactor (KUR–SANS), and carried out preliminary in-situ SANS experiments using $Ti_{0.31}Cr_{0.33}V_{0.36}$ alloy.

EXPERIMENTS: The $Ti_{0.31}Cr_{0.33}V_{0.36}$ alloy was prepared by arc-melting of a mixture consisting of Ti, Cr, and V in appropriate molar proportions. In-situ SANS experiments were carried out with the KUR–SANS installed at the CN–2 beam port of KUR [3]. The incident neutron wavelength was 0.28 nm.

RESULTS: Figure 1 shows the in-situ cell developed, which consists of a stainless steel body and two quartz windows (each 5 mm in thickness). In the in-situ cell, the $Ti_{0.31}Cr_{0.33}V_{0.36}$ alloy was hydrogenated up to H/M = 0.7 under a hydrogen atmosphere at around 1 MPa at room temperature. The in-situ SANS profile of $(Ti_{0.31}Cr_{0.33}V_{0.36})H_{0.7}$ during absorption is shown in Fig. 2. From the slope of the in-situ SANS profile in the q range 0.2–0.3 nm^{-1}, the fractal dimension of the particle-surface of $(Ti_{0.31}Cr_{0.33}V_{0.36})H_{0.7}$ was estimated to be 2.9, where q is the magnitude of a scattering vector.

In conclusion, we could establish the in-situ SANS technique for investigations of the hydrogen absorbing materials. We expect that the in-situ technique is absolutely beneficial to any intermetallic compound such as $LaNi_5$.

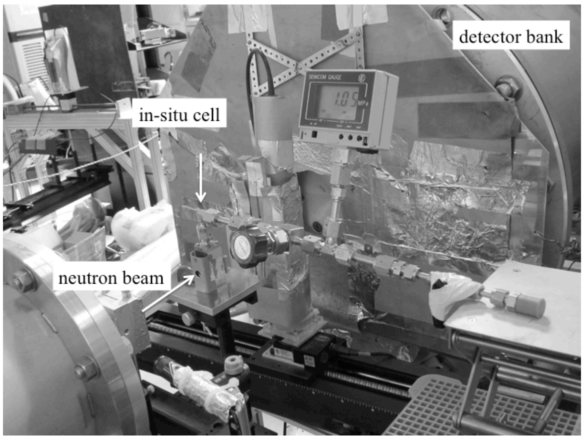

Fig. 1. The view of the high-pressure stainless steel cell for in-situ SANS experiments (in-situ cell), equipped with the KUR–SANS at the CN–2 beam port in KUR.

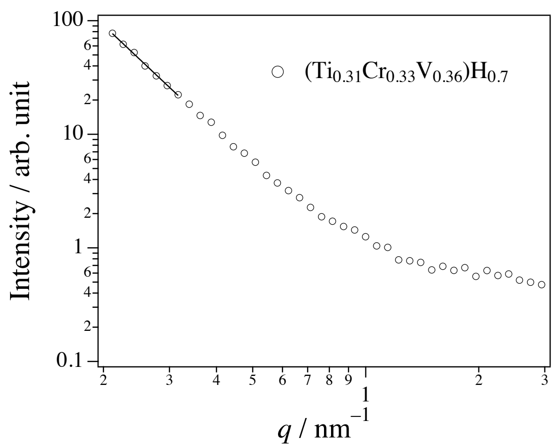

Fig. 2. In-site SANS profile of $(Ti_{0.31}Cr_{0.33}V_{0.36})H_{0.7}$ during absorption at room temperature. The solid line in the q range 0.2–3.0 nm^{-1} indicates the results of the least-squares fit obtained based on a power law.

REFERENCES:

[1] E. Akiba *et al.*, Intermetallics, **6** (1998) 461.
[2] R. A. Livingston, Cem. Concr. Res, **30** (2000) 1853.
[3] M. Sugiyama *et al.*, Jpn. J. Appl. Phys., **186** (1994) 6396.

採択課題番号 24P9-5　中性子小角散乱による Ti–Cr–V 水素吸蔵合金の表面観測　　プロジェクト
（京大・原子炉）森　一広、大場洋次郎、福永俊晴、杉山正明（京大院・工）市田智晴
（茨城大・工）岩瀬謙二

PR9-6

Small-Angle Neutron Scattering Analysis of Radiation-Fabricated Thermoresponsive Binary Hydrogels

N. Sato, Y. Oba and M. Sugiyama

Research Reactor Institute, Kyoto University

INTRODUCTION: Hydrogels are now widely used as useful biocompatible materials in a various fields of industry: medicine, food, hygiene products and other commodities. As well as in such an applicational aspect, polymer gels have also been attracting much attention in a scientific aspect. Network structure composed of interconnected polymer chains shows unique properties different from the original polymer and those properties are dependent on the gel characteristics such as crosslink density, structural inhomogeneity, electrical charge, and hydrogen bonding. Thermoresponsive property is one of those unique properties. Poly (*N*-isopropylacrylamide) (PNIPAm) in water shows coil-globule transition at ca. 34 °C. Inheriting this property, PNIPAm hydrogel shows volume transition at this temperature region: the gel is greatly shrinking when heated around 34 °C. Therefore it is quite interesting to fabricate multi-component gels composed of thermoresponsive component and other common hydrogel component.

Gel preparation utilizing ionizing radiation has a merit of high-quality gels. Radiation-prepared gels can be obtained only irradiating radiation such as γ-rays to the polymer solution, which needs no additives such as crosslinkers, reaction initiators, and catalysts.

In this study, we synthesized thermoresponsive porous binary hydrogels consisting of a common polymer, poly ethylene glycol (PEG) and PNIPAm by γ-ray irradiation. We revealed the structural characteristics of those gels below and above transition temperature employing small-angle X-ray and neutron scattering (SAXS, SANS) analysis.

In this report, the results of SANS experiments which were conducted at the Research Reactor Institute, Kyoto University is described.

EXPERIMENTS: A 10-wt% aqueous solution of PEG (MW 20000) was sealed in a vial after the bubbling with N_2 and then irradiated with γ-rays of 60 kGy at a dose rate of 1kGy/h. The obtained gels were purified by removing unreacted polymers with water rinsing several times. The purified PEG gels were swollen in 10-wt% NIPAm monomer aqueous solution. After removing water at the gel surface, the gels were irradiated again with γ-rays of 3 kGy at a dose rate of 1kGy/h. Then final product gels were obtained after removing unreacted NIPAm monomer and isolated PNIPAm chains. For the porous gels preparation, silica micro particles (hyprecica, 200 nm and 1000 nm) were incorporated before PEG gelation, which were decomposed by the hydrofluoric acid treatment after PEG gelation.

SANS experiments were carried out at the KUR-SANS facility. The neutron wavelength and the q-range were 0.28 nm and 0.16–3.5 nm^{-1}, respectively.

RESULTS: The SANS profile for the nonporous PEG/PNIPAm binary hydrogel at 20 °C is shown in Figure 1.

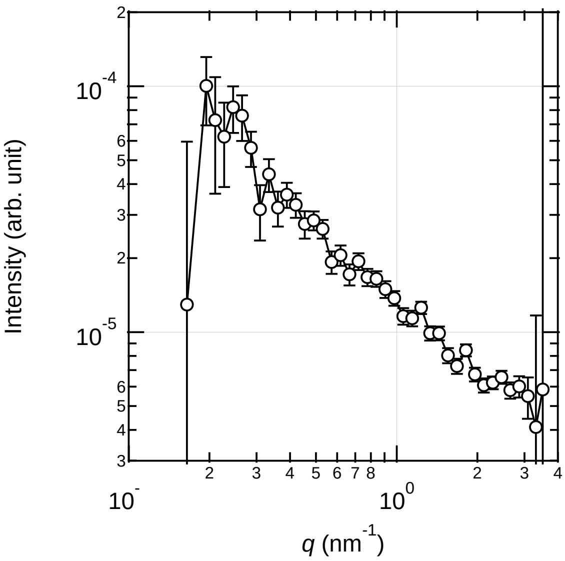

Fig 1. SANS profile of nonporous PEG/PNIPAm binary hydrogel at 20°C.

The gel is in the swollen state at this temperature. This profile resembles that of swollen pure PEG gels, and therefore the incorporated PNIPAm affects little binary gel structure in the swollen state.

At 40°C, in contrast, a steep rise in the low-q region appears for the binary gels. The slope of the rise for the porous gels has the relationship of $I \propto q^{-4}$, which is well-known equation Porod's law.

These results suggest the following scheme. When the temperature is lower than the transition temperature, the binary gels were swollen and the chains of each component polymer cannot be indistinguishable. At the temperature higher than the transition temperature, on the other hand, PNIPAm chains in the binary gels shrink while the PEG chains does not change. Especially for the porous gels, shrinking PNIPAm domains and PEG matrix domains are definitely separated. Since the Porod's law shows the presence of clear interface of two domains, it is indicated from this result that shrinking PNIPAm domains are formed in the still swollen PEG matrix and the borders of two domains appear at the higher temperature especially in the porous binary gels.

採択課題番号 24P9-6中性子小角散乱による感熱応答性多成分系高分子ゲルの構造解析プロジェクト
（京大・原子炉）佐藤信浩、杉山正明