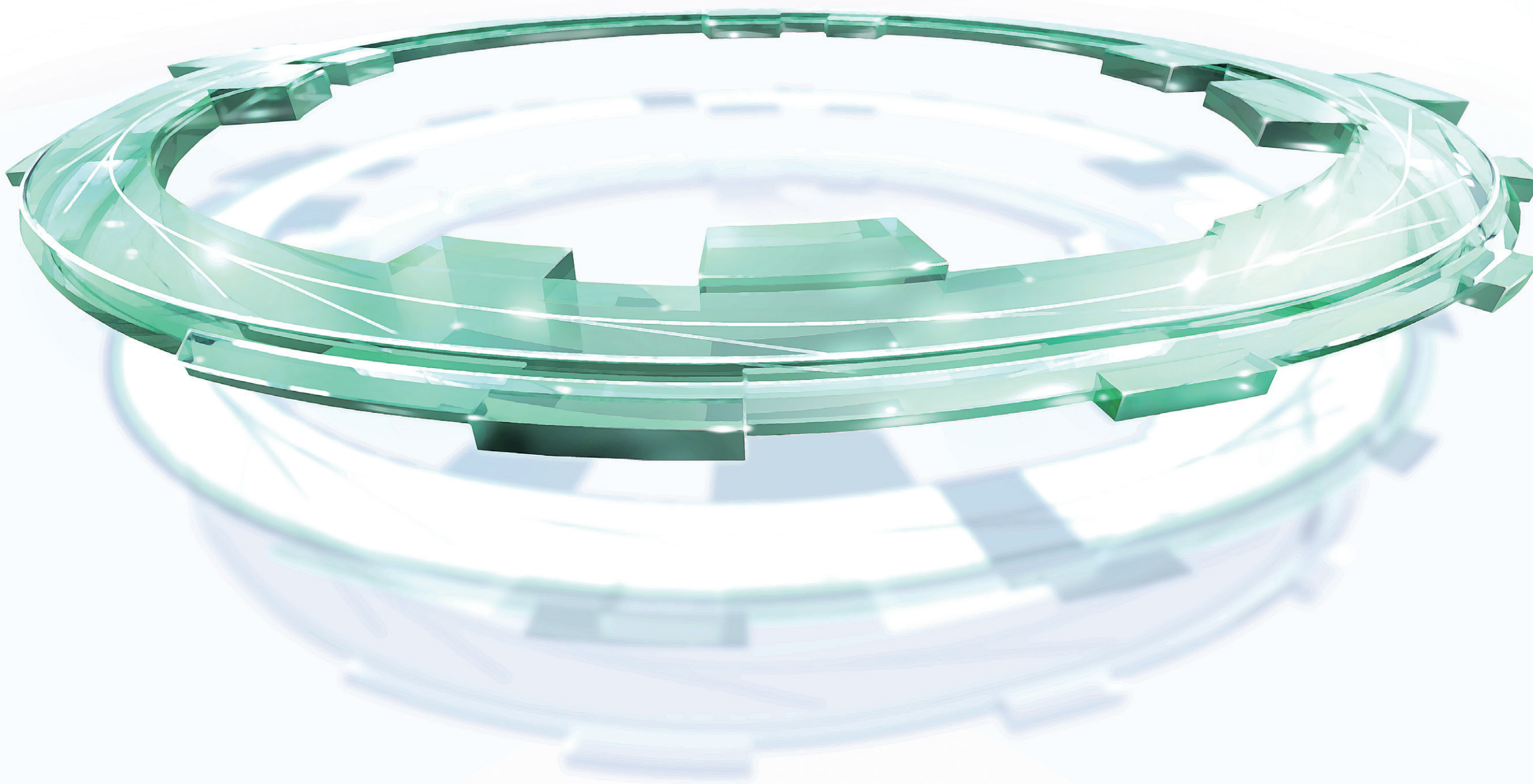




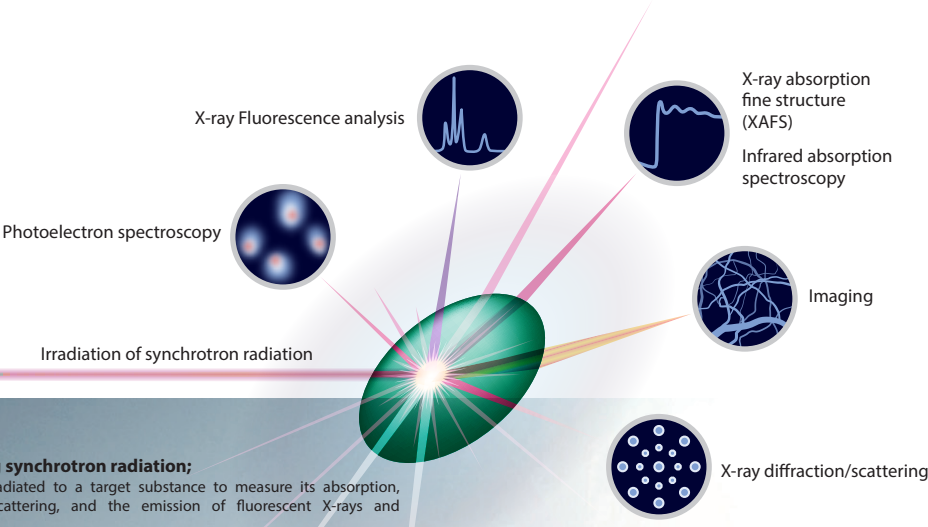
Registered Institution for Facilities Use Promotion
Japan Synchrotron Radiation Research Institute (JASRI)
phone +81-(0)791-58-2785 <http://www.spring8.or.jp/>

Successful Results of Industrial Applications at SPring-8

Greetings

In June 2019, I was inaugurated as the president of Japan Synchrotron Radiation Research Institute (JASRI), succeeding the former president, Dr. Yoshiharu Doi. Since SPring-8 was opened to users in 1997, I have carried out my research of the laboratory at the Univ. of Tokyo as a user of SPring-8, including joint research with industry groups. Although my relationship to SPring-8 has changed, I will endeavor to do my best to promote research activities at SPring-8/SACLA by fulfilling the mission of JASRI to select appropriate research proposals through a fair system and to support the research being conducted by users. Expectations regarding the use of SPring-8 for industrial applications are becoming increasingly prevalent in terms of giving back the achievements at SPring-8 to the general public. To fulfill these expectations, we will promote the use of SPring-8 for industrial applications through close information exchange with people from industry and also the dissemination of information related to the needs of people to use SPring-8 in industry and industrial applications. This brochure includes examples of industrial research activities carried out at SPring-8, the achievements of which are clearly understandable to those outside the field. I hope the brochure will help you understand the use of SPring-8 for industrial applications. I'm grateful to the people in industry who cooperated in editing this publication, as well as to all other people concerned.

Yoshiyuki Amemiya, President of JASRI



Research method using synchrotron radiation; synchrotron radiation is irradiated to a target substance to measure its absorption, transmission, diffraction, scattering, and the emission of fluorescent X-rays and photoelectrons.

CONTENTS

Realization of Environmentally-Friendly High-Performance Three-Way Catalyst	2
Clarification of two major mechanisms of catalysts for automotive exhaust purification	
<i>In situ</i> Imaging of Automotive Metallic Paints	4
Visualization of behavior of aluminum-flake reflective materials in paints	
Development of High Performance, Fuel-Efficient Tires	6
Analysis of three-dimensional structure in tire material at the nano to micrometer scale	
Development of Hair-Care Products from Rice Water	8
Visualizing the penetration of a protective compound into the hair using spectroscopy	
Development of Anti-Caries Chewing Gum	10
Crystallographic visualization of the process of restoration after early-stage caries	
Observation of Phase Behavior of Fat Crystals during Rapid Cooling	12
Elucidation of mechanism behind the formation of molecular compound	
CT Observation of State of Fine Ice Crystals in Frozen Foods	14
Quantitative evaluation of freezing method that keeps texture of foods	
Development of Silicone Rubber with Ultrahigh Tear Strength	16
Clarification of behavior of nanosilica filler aggregates	
Establishing Methods to Design Materials for Polymer-Modified Cement Waterproofing Coating	18
Pursuit of hydration and hardening processes	
Development of Material Design Method for Autoclaved Lightweight Aerated Concrete	20
Analysis of formation mechanism of crystalline component tobermorite	
Responding to the Restriction of Hazardous Substances in Electronic Products	22
Establishment of high-sensitivity nondestructive inspection method for hexavalent chromium	
Development of High-Efficiency Recycling Technology for Tungsten	24
Chemical state analysis of tungsten during ion exchange in collection system	
Development of Long-Life Next-Generation Li-Ion Batteries	26
Clarification of the causes of performance deterioration of Li-ion batteries	
Improvement of Capacity of Nickel-Metal Hydride Battery	28
Clarification of the optimal composition of the electrode	
Establishment of Method for Analyzing Next-Generation Metal-Oxide-Semiconductor Field-Effect Transistors	30
Nondestructive analysis of internal states of semiconductor laminated structures	
Accurate Analysis of Molecular Orientation of Organic Semiconductor Material	32
Clarification of excellent electric properties of transistor devices fabricated by vacuum deposition	
Research and Development of Stainless Steel with Hydrogen Embrittlement Resistance	34
Analysis of crystalline phase causing hydrogen embrittlement	
Establishment of Laser Peening Technology for Improving Surface Quality of Metallic Products	36
Optimization of laser irradiation conditions to enhance the effect of surface-quality improvement	
Suppression of Solidification Crack upon Steel Welding	38
The world's first successful two-dimensional time-resolved X-ray diffraction of metallographic changes in weld metals during real welding at a resolution of 0.01 sec.	
Control of Conditions of Finished Surface of Alloyed Hot-Dip Galvanized Steel Sheets	40
Elucidation of alloying reaction inside zinc coating	
SPring-8 contributes to the Development of Industries in addition to Academic Research.	42

The photograph shows the SPring-8 storage ring used to generate synchrotron radiation. Synchrotron radiation is an electromagnetic wave generated when a high-energy electron beam is bent in a magnetic field, and SPring-8 provides X-rays that are 100 million times brighter than conventional X-rays. Similarly to microscopes, the brighter the light, the higher the resolution.

Realization of Environmentally-Friendly High-Performance Three-Way Catalyst

Clarification of two major mechanisms of catalysts for automotive exhaust purification

Achievements

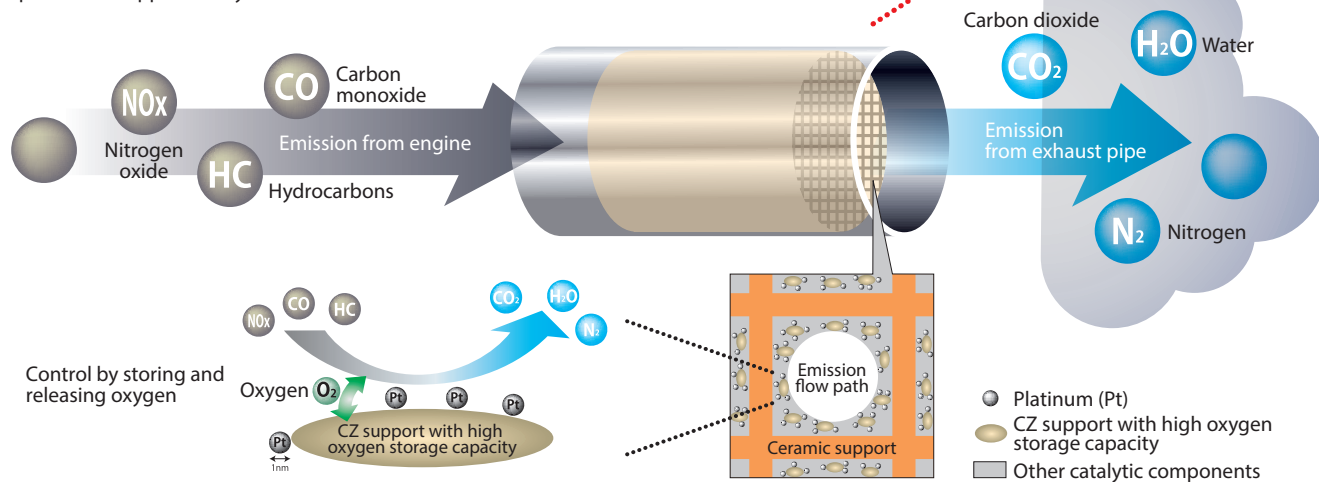
- Clarification of the **mechanism behind the storage and release of oxygen** to optimize the activities of **three-way catalysts*** for the purification of automotive exhaust gas
- Elucidation of the **aggregation suppression mechanism of catalytic noble-metal particles** to provide long-lasting catalytic activities
- Contribution to environmental cleanup by the installation of high-performance three-way catalysts developed using these analyses in gas-powered cars

R&D facility: Toyota Motor Corporation and Toyota Central R&D Labs., Inc.

***Three-way catalyst:** Harmful components in vehicular exhaust gas are oxidized or reduced by the action of catalysts and thus the exhaust gas is purified. Three-way catalysts promote the simultaneous detoxification of three harmful components, that is, carbon monoxide (CO), hydrocarbons (HCs), and nitrogen oxide (NOx), and are used most frequently in gasoline-powered vehicles. Three-way catalysts comprise noble metals causing catalytic reactions, supports for dispersing these noble metal particles in the nanometer scale, and catalytic promoters assisting the noble-metal-induced catalytic reactions.

Action of Pt/CZ-containing three-way catalyst

Emission purification devices (catalytic converters) are installed in exhaust pipes. The catalysts used in such devices contain platinum (Pt) as a noble metal and CZ (a solid solution of ceria CeO_2 and zirconia ZrO_2) supports as a catalytic promoter. These powdery catalytic components are trapped in a ceramic support with a honeycomb structure used to enlarge the area in contact with exhaust gas. CZ appropriately controls the concentration of oxygen and promotes the catalytic activity, while the aggregation of Pt particles is suppressed by the interaction between CZ and Pt.



Role of SPring-8

Background

The components of exhaust gas from automobiles are continuously changing; hence, to appropriately control the concentration of oxygen in accordance with the changing components, materials with a high capability to promptly store and release oxygen are required. CZ supports were developed as a material with such a function. However, the factors behind the improvement in the function were unknown.

Moreover, in the process of development, it was revealed that the aggregation of platinum (Pt) particles was suppressed by combining CZ supports with Pt, and thus the catalytic activity was maintained. We needed atomic-level analysis to clarify the mechanism behind this result.

Results

A high-brilliance, high-energy X-ray must be used to examine the structure of CZ supports in detail because their constituents are heavy elements. The results of the XAFS analysis at SPring-8 revealed that the ability of CZ supports to store and release oxygen varies depending on the arrangement of heavy metal atoms.

Moreover, the catalysts containing both CZ supports and Pt form Pt-O-Ce bonds when exposed to high-temperature exhaust gas, preventing the aggregation of Pt particles. The mechanism underlying this suppression of aggregation was clarified by XAFS analysis.

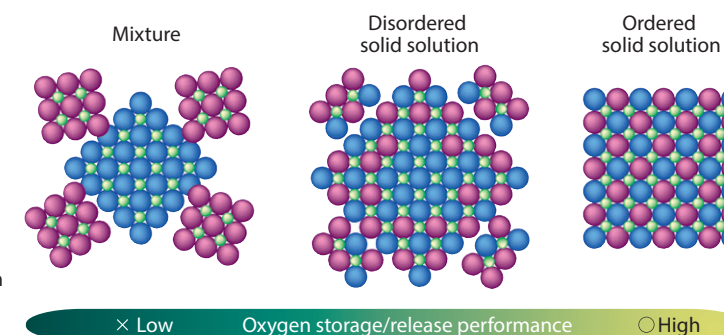
From these analyses, we succeeded in improving the catalytic materials containing Pt/CZ and in realizing a high-performance three-way catalyst.

Publication: Y. Nagai et al.; Catalysis Today **74**, 225-234 (2002) Y. Nagai et al.; Journal of Catalysis **242** (1), 103-109 (2006)
T. Tanabe et al.; Journal of Catalysis **257** (1), 117-124 (2008)

Relationship between structure of CZ support and oxygen storage/release performance

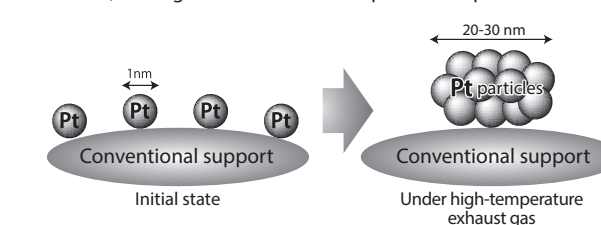
The significant effect of the atomic-level uniformity and configuration of Ce and Zr on the performance of storing and releasing oxygen was clarified. Subsequently, the mechanism of the deterioration of CZ supports was also clarified, and we elucidated a CZ support structure that sustains the high performance of storing and releasing oxygen over a long time (joint research with Kyoto University).

● Zr Zirconium
● Ce Cerium
● O Oxygen

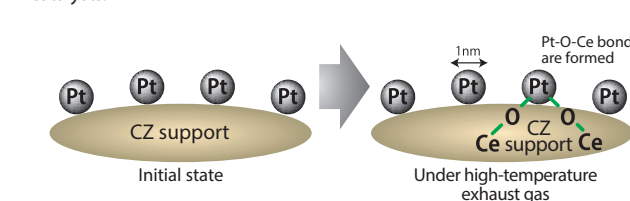


Suppression mechanism of catalytic noble-metal particle aggregation

When conventional catalysts are exposed to high-temperature gas, their Pt particles aggregate and grow. As a result, the surface area of the particles decreases, and hence the area in contact with exhaust gas decreases, causing a deterioration of the purification performance.



When Pt/CZ catalysts are exposed to high-temperature gas, Pt-O-Ce bonds are formed by the interaction between Pt and CZ, preventing the aggregation of Pt particles. Under normal conditions, catalytic reactions are induced when the bonds break, resulting in the lasting activity of the catalysts.



In situ Imaging of Automotive Metallic Paints

Visualization of behavior of aluminum-flake reflective materials in paints

Achievements

- The formation of coats of automotive **metallic paints*** was observed in the cross-sectional direction.
- It was confirmed through real-time observation that the orientation angle of **aluminum flakes**** changed with time after painting as a result of volumetric shrinkage and change in viscosity, although it remained unchanged immediately after painting.

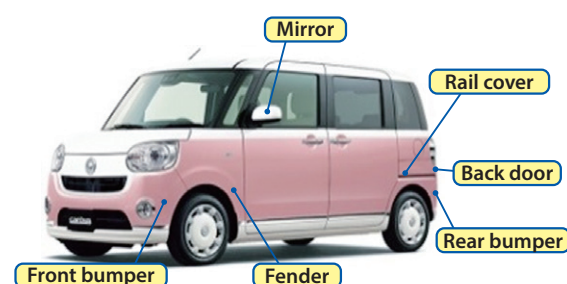
R&D institution: Daihatsu Motor Co., Ltd.

***Metallic paint:** Automotive paint is roughly classified into three types: metallic, pearlescent, and solid. Metallic and pearlescent paints contain fine aluminum and mica flakes and give characteristic colors that look different depending on the viewing angle.

****Aluminum flakes:** Aluminum flakes are metallic aluminum powder in the form of very thin flakes and one of the reflective materials used in paints. Aluminum flakes mixed with paints reflect light, and the shininess and color of the paints change with their orientation angle.

Example of color mismatch in production preparation stage

Use of resin in car body



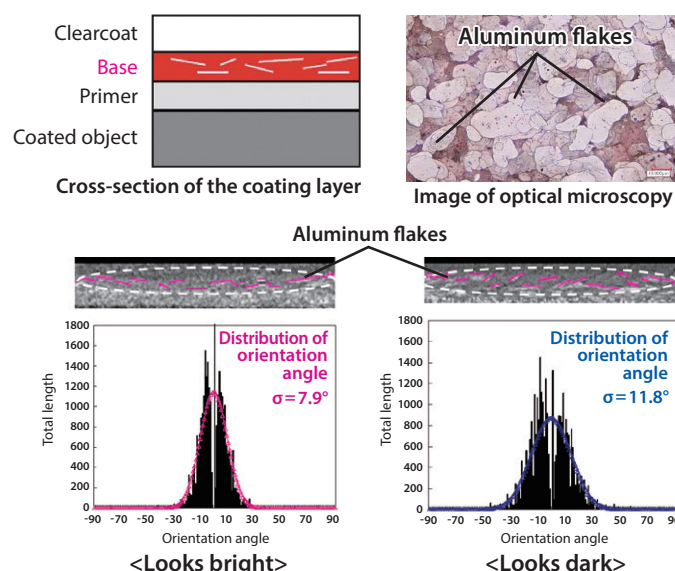
Color matching between door and fender

With the widespread use of resin for exterior parts to reduce the weight of car bodies, multiple attempts at painting and color matching have been required for paints containing aluminum-flake reflective materials (aluminum flakes) used on the steel sheets and resin of car bodies, as they are manufactured by different production processes. This is one of the causes of the long preparation time before automotive production.



Observation of cross section of paint by optical microscopy and SEM

SEM image and distribution of orientation angle of aluminum flakes



When the painted region was observed by optical microscopy, the overlapping of aluminum flakes was found but no clear differences in their orientation angle were seen.

Differences in the orientation angle of aluminum flakes were confirmed by SEM. However, there have been no methods for analyzing the behavioral changes of aluminum flakes during the formation of coats.

Role of SPring-8

Background

Recently, resin has been used in the exterior finish of cars in addition to steel sheets. Color matching between steel sheets and resin in metallic paints has been an issue to be addressed. Because the painting processes and materials used for steel sheets and resin differ, the orientation angles of fine aluminum flakes in metallic paints also differ, causing variation in the brightness and color of the paint. Therefore, a scientific approach to analyzing the mechanism underlying the behavior of aluminum flakes in detail has been required.

The difference in the coats cannot be clarified from the planar view obtained by optical microscopy. It has been clarified by scanning electron microscopy (SEM) that a difference in the distribution of the orientation angle affects the brightness of color. However, there have been no methods to analyze the behavioral changes of aluminum flakes during the formation of coats.

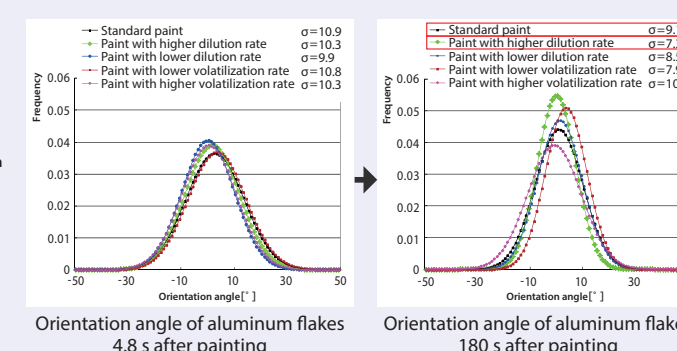
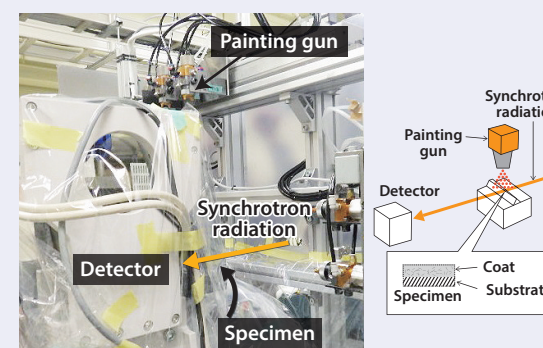
Results

The behavior of aluminum flakes was observed by X-ray imaging at SPring-8 using high-brilliance synchrotron radiation with high temporal and spatial resolutions. To observe the time course of paints under conditions close to those in the actual process, a setup for actual painting was installed at the experimental hutch.

It was found that the coats shrank with time after painting and that the orientation angle of aluminum flakes varied with the dilution and volatilization rates of the solvent, although the orientation angle did not vary immediately after painting. When the behavior of aluminum flakes was observed under the condition of multilayer painting, the viscosity of the paint changed in the painting process, which was considered to affect the behavior of the aluminum flakes. These findings are expected to shorten the preparation time before production in automotive production lines.

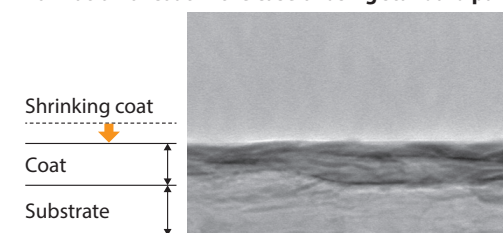
X-ray imaging at SPring-8

Experimental setup for painting installed at the experimental hutch of SPring-8

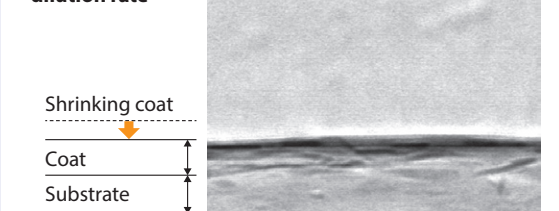


- The orientation angle of aluminum flakes changes with time.
- The change in the orientation angle depends on the painting conditions.

Formation of coat in the case of using standard paint



Formation of coat in the case of using paint with higher dilution rate



An experimental setup for painting was installed at the experimental hutch of SPring-8 BL46XU. To observe the dynamic behavior of aluminum flakes during the formation of coats, we applied a standard paint as well as paints with different dilution rates and volatilization rates to the substrate and compared the orientation angles of aluminum flakes 4.8 and 180 s after painting. It was found that the orientation angle of aluminum flakes during the formation of coats depended on the dilution and volatilization rates of the solvent.

Development of High Performance, Fuel-Efficient Tires

Analysis of three-dimensional structure in tire material at the nano to micrometer scale

Achievements

- Development of a **time resolved two-dimensional ultra-small angle X-ray scattering technique (2D-USAXS)** that can measure the three-dimensional structural information of silica nanoparticles in the rubber of tires
- By combining 2D-USAXS with **time resolved two-dimensional small angle X-ray scattering (2D-SAXS)***, development of a new material using molecular design based on the results of the two analyses
- Commercialization of high performance tires, with **rolling resistance**** reduced by 39% and fuel-efficiency improved by about 6% compared with their predecessors

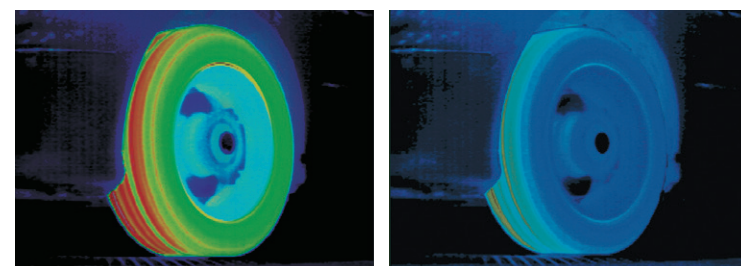
Research and development institution : Sumitomo Rubber Industries, Ltd.

***Time resolved two-dimensional small angle X-ray scattering (2D-SAXS):** A method for measuring the size and shape of structures smaller than several hundred nanometers (nm: 10^{-9} m) within substances. The BL03XU completed in 2011 by the Advanced Softmaterial Beamline Consortium and the BL40B2 Structural Biology Beamline II public beamline were used for measurement.

****Rolling resistance:** A force that acts in the opposite direction to the direction of travel of the tire. This involves three factors, air resistance, ground friction, and tire deformation, but tire deformation accounts for about 90%.

Thermographic capture comparing the temperatures of the tire surfaces when driving

Much of the former tire is orange and yellow, indicating high temperatures. The low temperature of the new product reflects its excellent mileage performance.

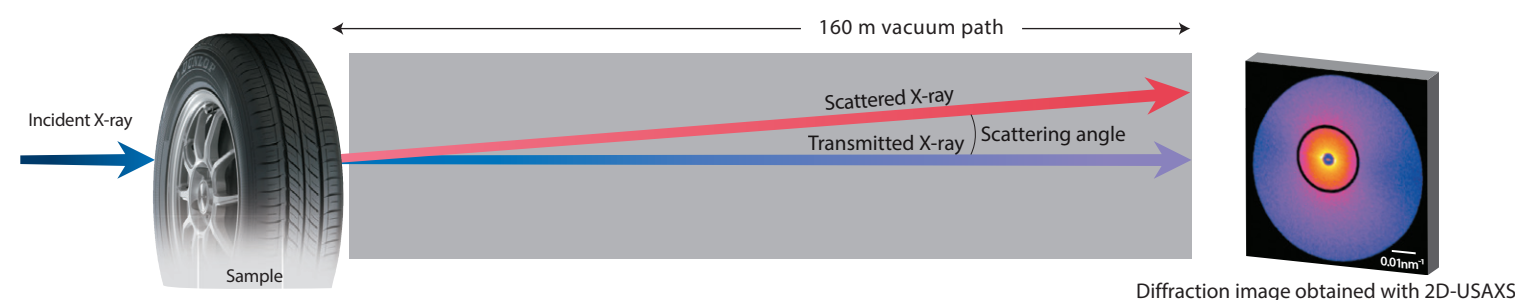


Former tire

Newly developed fuel-efficient tire

Time resolved two-dimensional ultra-small-angle X-ray scattering (2D-USAXS)

A method for measuring the size and shape of structures in the submicrometer range (10^{-7} m) within substances. By making the 160 m long vacuum path of the BL20XU the camera length, it was possible to observe X-rays scattered at an extremely low angle of less than $1/100,000$ to analyze the structures in this range. As a result, we could identify the network structure formed by the silica particles in the rubber.



Diffraction image obtained with 2D-USAXS

Role of SPRing-8

Background

The **fuel-efficiency of tires** has a significant effect on improving the fuel-efficiency of vehicles. Incidentally, deformation of the tire against the road surface results in gripping performance through energy loss, thereby making driving safer.

Generally the main material of tires is rubber, but adding nanoparticles of carbon or silica increases their strength and enables the development of tires that resist deformation and have high grip. However, raising gripping performance increases energy loss, which reduces mileage performance. This was thought to be because the nanoparticles in the rubber cohere in a network configuration, but there was no method of investigating structures in this submicrometer range.

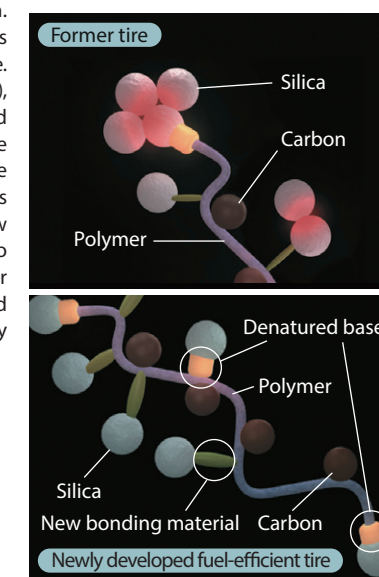
Results

First, we developed a time resolved two-dimensional ultra-small-angle X-ray scattering method (2D-USAXS) that can measure the submicrometer range using the high-brightness, highly parallel X-ray at SPRing-8, and observed the network structures formed by silica particles in the rubber at the SPRing-8 site. Then we conducted molecular level measurement in the nanometer range, and from the two sets of data, we identified the part of the **silica network structure** that increases frictional force and reduces mileage performance.

In addition to this experiment, we carried out molecular design reflecting the result of simulation in which temporal change is applied to the network structure to develop a new material, with a structure in which the silica particles are dispersed. This gave rise to a high performance tire with outstanding grip and fuel-efficiency.

Comparison of the molecular bonds in rubber

The rubber of tires is composed of synthetic rubber, natural rubber and a stiffener. In the former tires (top), there are few links, which is a factor in heat generation. In addition, the silica coheres to form a network structure. In the new product (bottom), a "both-ends-modified polymer" is used as the synthetic rubber. The denatured bases at the ends of the polymer and the new bonding material work to improve the bonding power of the silica and polymer, and to increase the dispersibility of the silica.



Development of Hair-Care Products from Rice Water

Visualizing the penetration of a protective compound into the hair using spectroscopy

Achievements

- Development of a technique to observe the penetration of a protective ingredient into the hair
- Demonstration of the effect of inositol, an ingredient of rice water, on protection and beautification of the hair
- Development of new hair-care products containing inositol

R&D facility: Kracie Home Products, Ltd.

***Fluorescence imaging:** An observation technique using fluorescence microscopes to detect fluorescently-labelled molecules, such as fluorescein isothiocyanate, that have been introduced into proteins.

****Infrared microspectrometer:** This device combines features of an infrared spectrophotometer and microscope; it can measure the distributions of test ingredients. Powerful infrared synchrotron radiation available at the SPring-8's Infrared Materials Science (BL43IR) beamline allows detailed measurements of the distributions of ingredients in the cross-section of individual hairs.

Role of SPring-8

Background

Evaluation of modern hair-care products requires not only characterization of sensory features, such as improvement in the feel and gloss of the hair, but also scientific explanation of the mechanisms by which the active ingredients exert their effects. Inositol, a carbohydrate contained in rice water, has been used as a hairdressing in Japan since the 8th century. This compound has been demonstrated to have protective and beautifying effects on the hair.

Fluorescence imaging* has been used to observe the penetration processes of the active ingredient as it exerts its hair-beautifying effects. However, the quantification of the effects was difficult, and inositol's hair-beautifying mechanisms remain unknown.

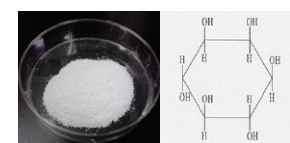
Results

The **infrared microspectrometer**** at SPring-8, which uses infrared synchrotron radiation, can examine the subtle differences between the interiors of healthy and damaged hair. Examination of hair onto which inositol was applied revealed that signals originating from chemical bonds specific to inositol are stronger near the hair surface, but decrease toward the hair center, indicating that inositol penetrates into the hair gradually. Additionally, we demonstrated that inositol stays inside the hair, allowing its protective and beautifying effects to persist even after rinsing.

Based on this result, new hair-care products containing inositol are being developed. The wisdom of ancient people has contributed extensively to these developments.

Hair-protective and -beautifying effects of inositol

Inositol, which is an ingredient of rice water, has the capability to repair damaged hair, as well as protect the hair from damage.

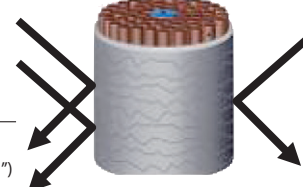


Protective effects

Damages

- 1) Surface (Hair dye)
- 2) Inside (Permanent wave, "Perm")

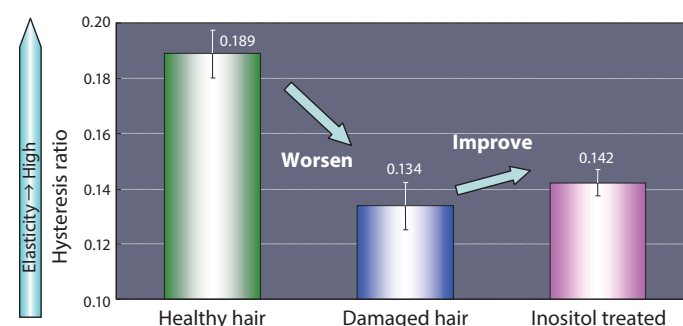
Inositol



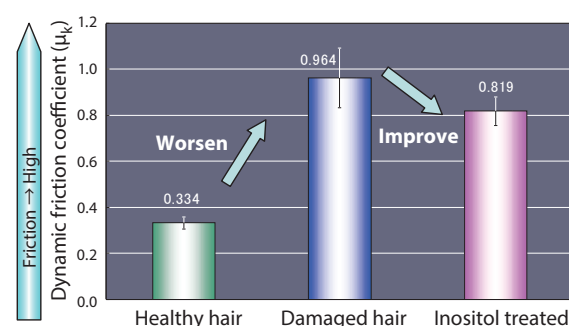
Protective effects

Damage-promoting factor

- 3) Surface friction (While rinsing)



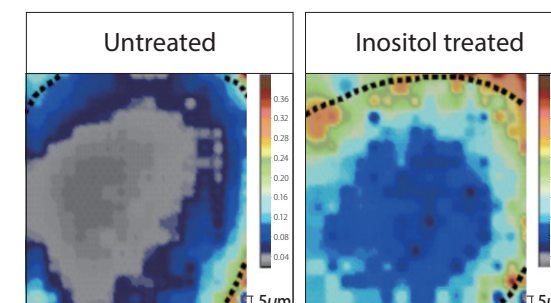
Suppressing the worsening of hair elasticity due to damage from perms (Protection).



Suppressing damage from friction during rinsing (Protection).

Permeability of inositol into the hair

Numbers in the legend of the figures below represent the absorption intensity of infrared synchrotron radiation. A larger number indicates that there are more chemical bonds specific to inositol. The figure on the right, in which warm colors are highly visible, shows that the inositol concentration is higher along the outer contour of the hair (dashed line). This is the first-ever quantitative visualization of the penetration and persistence of inositol, a hair-protecting ingredient, into the hair.



Inositol stays inside the hair even after rinsing, resulting in continuing protective hair-beautifying effects!



Development of Anti-Caries Chewing Gum

Crystallographic visualization of the process of restoration after early-stage caries

Achievements

- First observation of crystal-structure changes involving **demineralization** and remineralization associated with **early-stage caries*** (tooth decay)
- Restoring lost crystals by supplying **phosphoryl oligosaccharides of calcium**** in cases of early-stage caries
- Development and commercialization of anti-caries chewing gum[†] containing phosphoryl oligosaccharides of calcium

R&D facility: Ezaki Glico Co., Ltd.

[†] This anti-caries chewing gum is approved as a Food for Specified Health Use (September 30, 2010)

***Early-stage caries:** Oral bacteria produce acids from carbohydrates contained in food, and these acids decay tooth crystals composed of phosphorus and calcium (**demineralization**). This mineral loss is termed early-stage caries. **Remineralization**, which refers to the process of restoring minerals lost in demineralization, allows recovery from early-stage caries.

****Phosphoryl oligosaccharides of calcium:** Phosphoryl oligosaccharides of calcium is a mineral that can be produced from potato starch. The compound is highly soluble in saliva. Caries-causing bacteria cannot use this compound to produce acids that cause caries.

Tooth structure and early-stage caries

In the early-stage caries, minerals inside the enamel are eroded (demineralization) and the demineralized area becomes cloudy compared to the surrounding healthy area. At this stage, if phosphate and calcium ions in saliva are supplied to the demineralized area, remineralization can be induced.

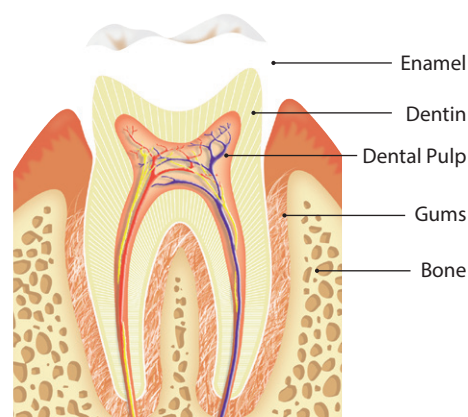
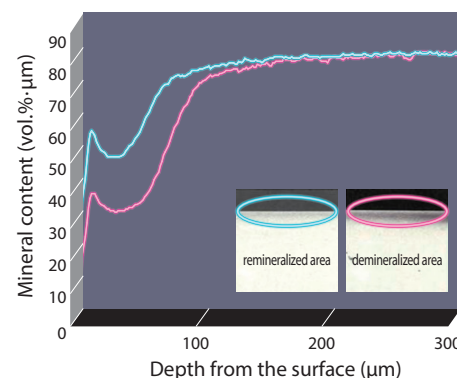


Demonstration of recrystallization induced by phosphoryl oligosaccharides of calcium

Changes in mineral content

Measured using conventional transversal microradiography

Mineral content decreases in the demineralized area (red), while it is restored in the remineralized area (blue).



Role of SPring-8

Background

When early-stage caries advances, the tooth surface is eroded and tooth cavities (cariou pits) develop. Tooth drilling is required to treat these cavities; therefore, preventive care such as regular tooth brushing has been recommended to remove caries-causing plaque.

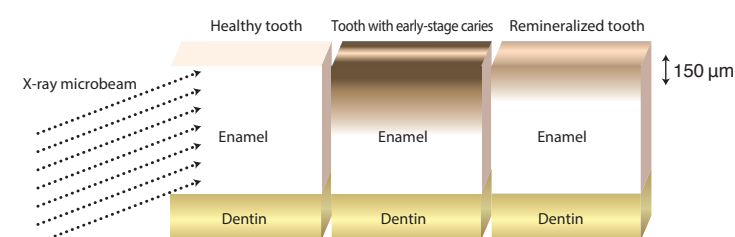
Recently, research on regenerating minerals eroded during demineralization, remineralization, has been conducted. These studies revealed that phosphoryl oligosaccharides of calcium, a relatively recently synthesized compound, can facilitate remineralization on the tooth. However, conventional experimental techniques can only evaluate changes in quantitative factors such as mineral content and hardness of the tooth; they cannot measure detailed changes in crystallization that determines the strength of the tooth. For these latter purposes, we turned to X-ray crystallographic studies.

Publication: N. Yagi et al.; Journal of Synchrotron Radiation **16** (3), 398-404 (2009)
T. Tanaka et al.; Caries Research **44** (3), 253-259 (2010)

Results

Tooth crystals are eroded on scales of ~0.1 mm in early-stage caries; therefore, measurement at the micrometer (μm) level is required in order to examine **changes in the crystals**. Such fine measurements can only be achieved using X-ray microbeams at SPring-8. To this end, early-stage caries were experimentally generated on enamel samples extracted from bovine teeth; these samples were then subjected to remineralization for a certain period of time in human oral cavities. Remineralization was achieved through the chewing of gum that contained phosphoryl oligosaccharides of calcium. Healthy, demineralized, and remineralized areas were then analyzed using X-ray microbeams.

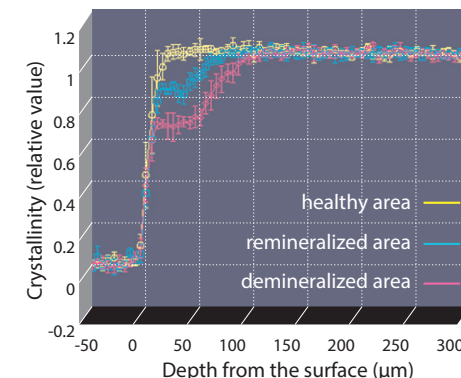
This experiment revealed that demineralization occurs at the crystal level but not at the atomic level, the amount of crystals as well as mineral content in the remineralized area increases, and the crystals are oriented in the same manner found in a healthy tooth.



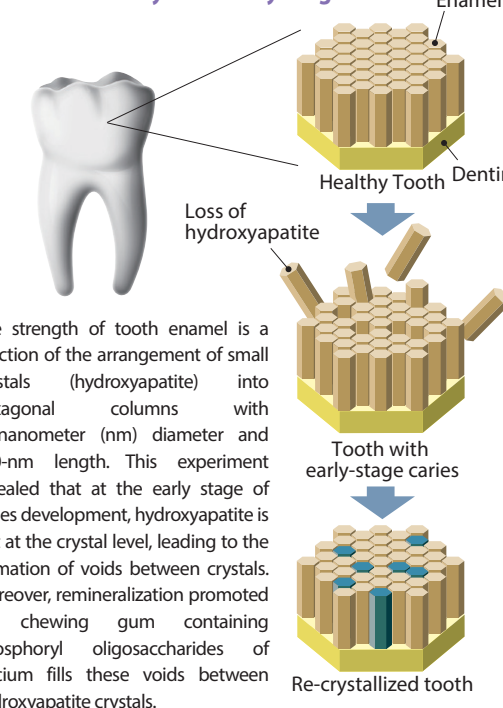
Changes in crystallinity

Measured using X-ray microbeams at SPring-8

Crystallinity of the demineralized area (red) is degraded compared to the healthy area (yellow), while crystallinity in the remineralized area (blue) is restored.



Phosphoryl oligosaccharides of calcium can facilitate recovery from early-stage caries



The strength of tooth enamel is a function of the arrangement of small crystals (hydroxyapatite) into hexagonal columns with 20-nanometer (nm) diameter and 100-nm length. This experiment revealed that at the early stage of caries development, hydroxyapatite is lost at the crystal level, leading to the formation of voids between crystals. Moreover, remineralization promoted by chewing gum containing phosphoryl oligosaccharides of calcium fills these voids between hydroxyapatite crystals.

Observation of Phase Behavior of Fat Crystals during Rapid Cooling

Elucidation of mechanism behind the formation of molecular compound

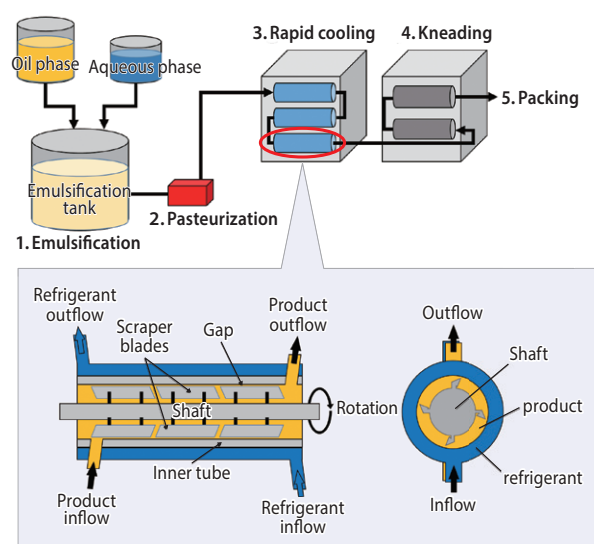
Achievements

- *In situ* observation of phase behavior and polymorphic changes of fat crystals during rapid cooling in margarine manufacturing process
- Determination of cooling rate and post-cooling heating temperature required for the formation of **molecular compound (MC)***
- The formation of MC will be controlled by adjusting the manufacturing conditions

R&D Institution: Miyoshi Oil & Fat Co., Ltd.

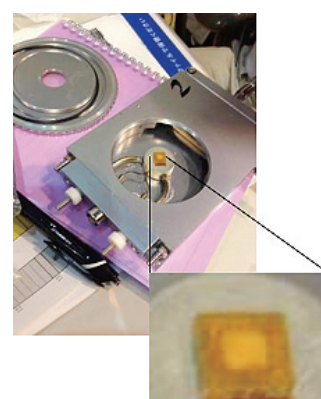
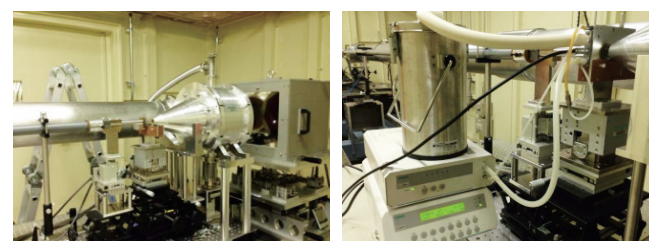
*MC: Molecular compound crystal formed by binding different molecules at a certain ratio. Its properties are different from those of their component molecules. POP and OPO, the main components of palm oil and pork lard, respectively, form MC at a ratio of 1:1.

Manufacturing process of margarine



Margarine is manufactured by emulsifying the oil and aqueous phases, pasteurizing, rapidly cooling, kneading, and packing. In the process of rapid cooling and kneading, the product is cooled by a scraped-surface heat exchanger. The cooling rate is estimated to be at least 100 °C/min.

Time-resolved X-ray diffraction measurement at SPring-8



Time-resolved X-ray diffraction measurement was carried out using a small-angle scattering device at BL19B2. The sample was cooled slowly (5 °C/min) and rapidly (40 °C/min) from 100 to -50 °C using liquid nitrogen. Next, it was heated at a rate of 10 °C/min from -50 to 100 °C.

Role of SPring-8

Background

Recently, it has been reported that the consumption of foods with high contents of saturated and trans fatty acids increases the risk of diseases such as myocardial infarction and diabetes. However, oil and fat products such as margarine are required to have some degree of firmness for consistency and plasticity. If the contents of the saturated and trans fatty acids are decreased, the properties of oil and fat products will greatly change.

We focused on the MC as a means of solving the above problem. The MC crystals are rich in oleic acids, giving them a healthy image, and have moderate hardness because they are solid at room temperature. Thus, we expect to use them as alternatives to saturated and trans fatty acids. However, their crystal phase behavior during rapid cooling at a rate of ≥ 100 °C/min in the manufacturing process has not yet been clarified.

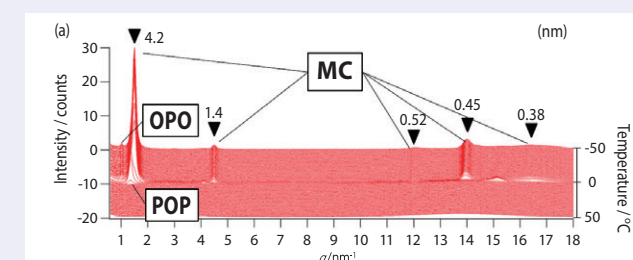
Results

In a preliminary experiment, we prepared a sample of MC crystals by mixing 1,3-dioleoyl-2-palmitoyl glycerol (OPO) and 1,3-dipalmitoyl-2-oleoyl-sn-glycerol (POP) at a ratio of 1:1 and measured a thermogram by differential scanning calorimetry (DSC) while changing the cooling rate. The thermogram clearly shows that the formation of MC greatly depended on the cooling rate and drastically changed at 40 °C/min and above.

Next, time-resolved X-ray diffraction measurement was carried out using high-brilliance synchrotron radiation at SPring-8, which enables the continuous observation of the behavior of fat crystals as they quickly change over a few seconds, as follows. The sample was cooled slowly (5 °C/min) and rapidly (40 °C/min). Next, it was heated (10 °C/min). The analysis of the phase behavior and polymorphic changes of the sample revealed the cooling rate required to form MC and the optimum temperature for its efficient formation. Therefore, the MC formation can be controlled by adjusting the cooling rate and product temperature.

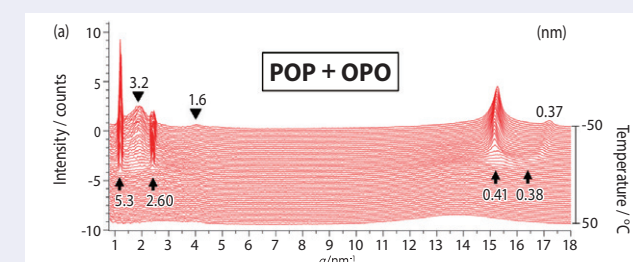
X-ray diffraction measurement under different cooling and heating conditions

A sample was prepared by mixing POP and OPO, the main component of palm oil and lard, respectively, at a ratio of 1:1. Time-resolved X-ray diffraction measurement was carried out during slow and rapid cooling and also during heating in the temperature range from -50 to 100 °C. We analyzed the phase behavior and polymorphic changes of MC crystals during cooling and heating. The results suggest the possibility of controlling MC formation by adjusting the cooling rate.



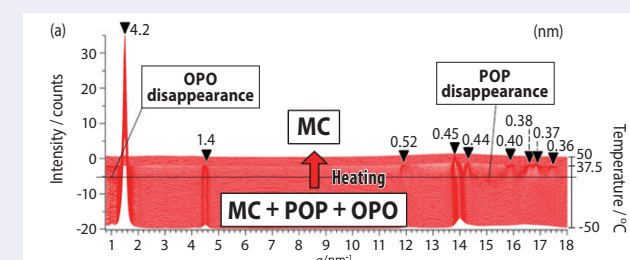
(1) Cooling rate, 5 °C/min

Strong diffraction peaks of MC crystals were observed, confirming that the MC was formed during slow cooling. Moreover, weak diffraction peaks of POP and OPO crystals were also observed, indicating that some of the POP and OPO were independently formed.



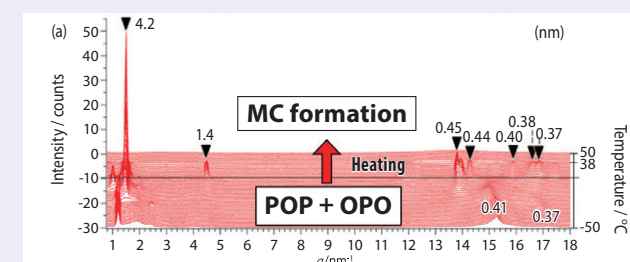
(2) Cooling rate, 40 °C/min

No diffraction peaks of MC crystals were observed, indicating that no MC was formed during rapid cooling.



(3) Heating at 10 °C/min after slow cooling at 5 °C/min

The weak diffraction peaks of POP and OPO crystals disappeared upon heating. This indicates that the POP and OPO transformed into MC.



(4) Heating at 10 °C/min after rapid cooling at 40 °C/min

As the diffraction peaks of POP and OPO crystals weakened, diffraction peaks of MC crystals started to appear and increased in the intensity while heating. This suggests that the POP and OPO that had formed independently transformed into MC upon heating.

CT Observation of State of Fine Ice Crystals in Frozen Foods

Quantitative evaluation of freezing method that keeps texture of foods

Achievements

- Fine ice crystals in foods frozen by a home refrigerator with an instantaneous freezing function based on supercooling* were successfully observed by high-brilliance X-ray computed tomography (CT).
- Conventionally, frozen foods have mainly been evaluated after thawing, but a quantitative evaluation method using high-brilliance X-rays have been developed for frozen foods before thawing. The effects of freezing technology on the growth of ice crystals in foods have been confirmed.

R&D institution: Mitsubishi Electric Corporation

***Supercooling:** The unstable state in which substances such as water exist as liquids even at temperatures lower than its freezing point. For example, supercooled water exists as a liquid even below 0 °C.

****SUNBEAM:** Contract beamlines at SPring-8 managed by the SUNBEAM Consortium consisting of 13 companies. There are two beamlines: an insertion device (ID) beamline (BL16XU) and a bending magnet (BM) beamline (BL16B2).

Principle of freezing based on supercooling

When water starts to freeze, ice nucleus forms. Then ice crystals grow around the ice nucleus. Conversely, water will not freeze even at a temperature lower than its freezing point (0 °C) unless an ice nucleus forms. When a fluctuation in temperature or an impact is applied to supercooled water, an ice nucleus abruptly forms and the freezing process occurs throughout the water upon the formation of ice nucleus. The ice crystals that form in supercooled water are smaller than those frozen conventionally.

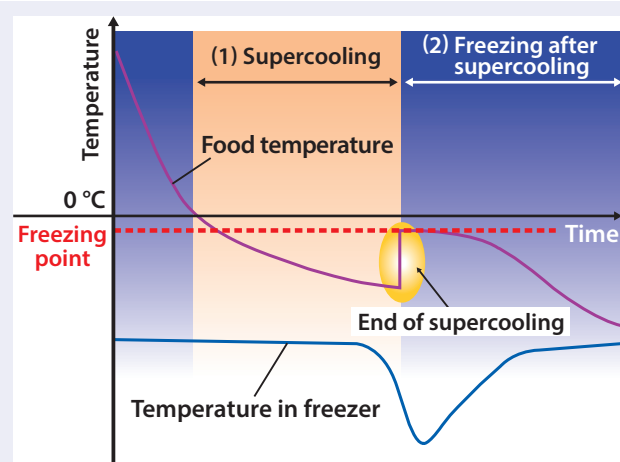
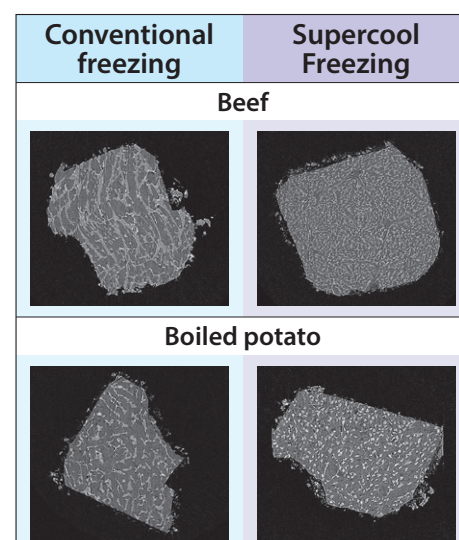


Diagram of transition of temperature in supercooling and subsequent freezing

CT imaging at BL19B2

Beef (upper) and boiled potato (lower) frozen by conventional freezing (left) and Supercool Freezing (right) were compared. The regions with bright contrast are food fibers or proteins, whereas the regions with dark contrast are ice crystals. The ice crystals are distributed more widely in the samples frozen by Supercool Freezing than those frozen by conventional freezing. It was demonstrated that smaller ice crystals have less effect on the tissue structure of frozen foods.



Role of SPring-8

Background

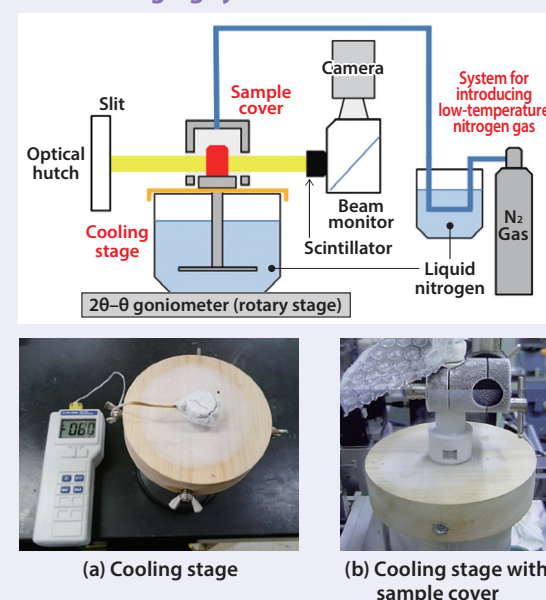
When frozen foods such as meats, fishes, and vegetables thaw, losses of moisture, called drips, from foods often occur because ice crystals grown in foods break the cell tissue of the foods. Drips is considered to deteriorate tastes of foods after thawing. To solve this problem, an instantaneous freezing technique called Supercool Freezing, which is based on supercooling, was developed. It was found that ice crystals in foods frozen by Supercool Freezing are smaller than those in foods frozen by conventional freezing. Smaller ice crystals have a significant effect on suppressing drips and maintain the texture of foods. Methods to measure quantitatively the size of ice crystals in frozen foods are required. The conventional methods involve indirectly observing pieces of stained or frozen/dried foods with limited applications for food samples. Therefore, direct nondestructive methods for observing the state of ice crystals in entire food samples have been required.

Results

X-ray CT is effective method to observe the internal state of substances nondestructively. However, conventional X-ray CT equipment using a wide energy band of X-ray are unable to distinguish substances with small differences of X-ray absorption coefficients, such as foods and ice crystals.

High-brilliance monochromatic X-rays at SPring-8 enables detailed imaging of the internal state of substances such as foods and ice crystals. We carried out a preliminary experiment at BL19B2 (Engineering Science Research I), which is well equipped with sample freezing systems. Afterwards, we introduced a frozen imaging system at BL16B2 of **SUNBEAM****. Using these systems, beef, tuna, and boiled potato, which were frozen with Supercool Freezing and conventional freezing, were photographed while being continuously rotated by 180° to obtain a few hundred tomographic images. The cross-sectional images of the ice crystals were compared accordingly to the freezing methods. Supercool Freezing leads to smaller size of ice crystals and less distort tissues of foods than conventional freezing methods.

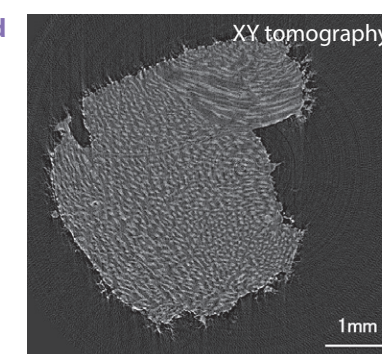
Frozen imaging system at BL16B2



A holder containing a frozen food was placed on a rotary sample stage set in the experimental hutch and three-dimensionally photographed by X-ray CT system. A equipment blowing low-temperature nitrogen gas to samples was set at the upper cover of the holder to prevent thawing of the ice and frost on the holder during photography. This system enabled us to continuously obtain images at intervals of 250 ms while keeping the temperature of samples at approximately -30 °C and rotating the stage by 180° at a rate of 2.2°/s.

CT image obtained at BL16B2

The CT image of a frozen beef indicates that the sample can be clearly photographed with negligible thawing and little frost during observation.



Refrigerator with Supercool Freezing function

This series of refrigerators first appeared on the market in 2007, and such refrigerators with improved functions are still commercially available.

Development of Silicone Rubber with Ultrahigh Tear Strength

Clarification of behavior of nanosilica filler aggregates

Achievements

- Clarification of the change in the hierarchical structure of nanosilica filler aggregates along with the elongation of **silicone rubber***
- Marked improvement of hardness, tear strength, and independent control of the elongation of silicone rubber
- Development of silicone rubber with high tear strength while maintaining transparency

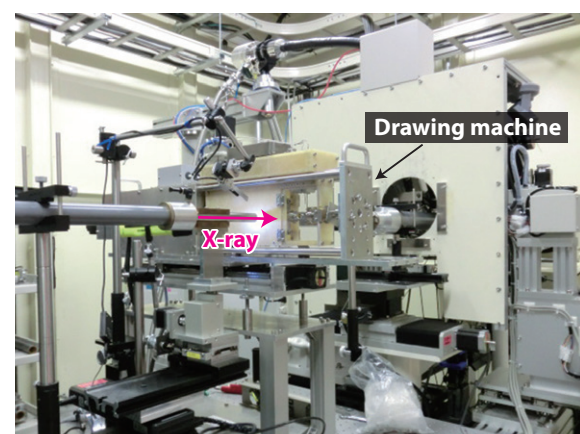
R&D facility: Sumitomo Bakelite Co., Ltd.

***Silicone rubber:** Silicone rubber mainly consists of silicon and contains siloxane bonds (SiO) of alternately bonded silicon and oxygen. It has various characteristics such as resistance to high and low temperatures. Silicone rubber has been widely used as a medical material. The development of a material that has high transparency, moderate hardness, and a high tear strength is demanded.

****Small-angle X-ray scattering (SAXS):** SAXS is a technique for analyzing the nanoscale structure of a target specimen using the scattering intensity profile obtained by irradiating the specimen with X-rays.

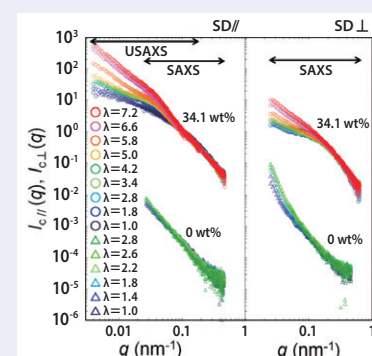
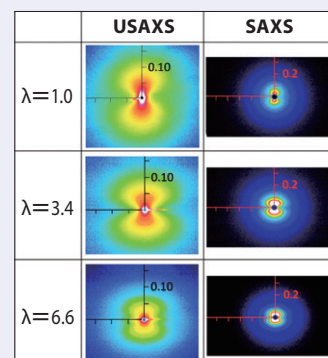
*****Ultras-small-angle X-ray scattering (USAXS):** Conventional SAXS can generally identify a structure with a size of 2–30 nm. USAXS is a technique for measuring and evaluating a mesoscopic structure with a size of 200–300 nm using the scattering intensity profile in a range of ultrasmall angles.

Ultrahigh-speed tensile test and SAXS using BL19B2



Stress relaxation starts to occur simultaneously when silicone rubber is elongated. The state of the aggregation of the filler inside the silicone rubber was observed while the silicone rubber was extended using a drawing machine with a maximum speed of 1 m/s.

X-ray two-dimensional USAXS and SAXS images of silicone rubber with nanosilica filler



Intensity profile in the direction parallel to elongation of silicone rubber (filler content, 34.1 wt%; λ , elongation factor).

A characteristic pattern indicating the orientation was observed from the beginning of elongation. The state of the aggregation of the filler elongated in the elongation direction of the silicone rubber was clarified.

Role of SPring-8

Background

With the advancement of medical care, the development of medical equipment with higher performance has been required. Among the various medical materials, silicone rubber has superior resistance to high and low temperatures, chemical stability, electrical insulation, gas permeability, transparency, and a mold release characteristic. However, the tear strength and tensile strength of silicone rubber are inferior to those of other rubber materials and the range of its application has been limited.

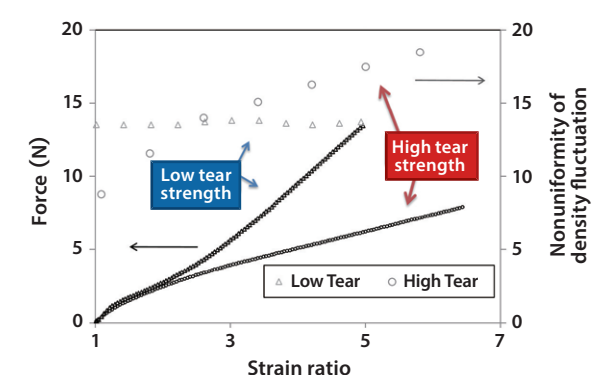
Under such circumstances, the development of transparent silicone rubber with a high mechanical strength has been required. To realize such a rubber, a nanosilica filler was dispersed in silicone rubber as a reinforcing material and the bonding between the nanosilica filler and the surrounding rubber was strengthened to improve the mechanical strength of the silicone rubber. It was also required to clarify the relationship between the structure of the filler aggregate and the tear strength upon the elongation of silicone rubber.

Results

SAXS** and **USAXS***** were used to observe the dispersion state of the filler, including the aggregation structure. The beamline of SPring-8 is appropriate for evaluating structures with a wide size range. *In situ* observation of the hierarchical structure and the behavioral change of nanosilica aggregates was carried out by SAXS at SPring-8 while silicone rubber specimens with a dispersed nanosilica filler and different strengths were elongated using a tensile tester.

The results indicate that when silicone rubber with strong bonding between the filler and the matrix is elongated, the filler aggregates are also elongated in the same direction, which leads to an increase in the tear strength. In addition, the strength of the interface depends on the state of the aggregation of the filler. This finding has led to the improvement of the property of silicone rubber by controlling the state of the aggregation.

Differences in stress and nonuniformity of density fluctuation depending on tear strength

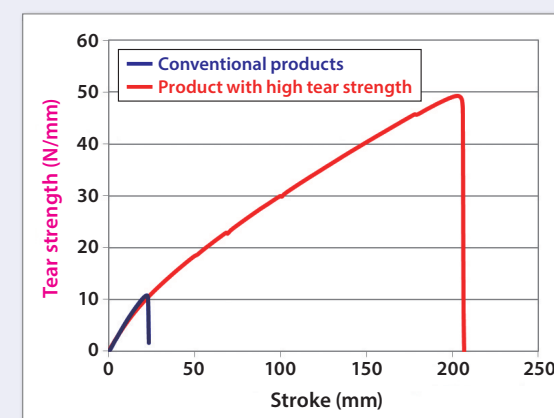


When the bonding between the filler and the matrix is strong, the tear strength is high.



Example of product using silicone as a medical material: unit for continuous suction of blood, pus, and effusion from wounded area after surgery

Developed silicone rubber with high tear strength



The surface of the filler was treated to improve the interface strength between the filler and the silicone on the basis of the observed change in the state of the aggregation of the nanosilica filler upon elongation. The research group has succeeded in developing silicone rubber with a tear strength that is approximately fivefold (50 N/mm) that of conventional silicone rubber over a wide range of hardness of 30–70 (product name, DuraQ®). It is expected that this ultrahigh-tear-strength silicone rubber will be used as a material not only in medical equipment but also in mechanical parts of automobiles and airplanes, clothing, healthcare products, and wearable products.

Establishing Methods to Design Materials for Polymer-Modified Cement Waterproofing Coating

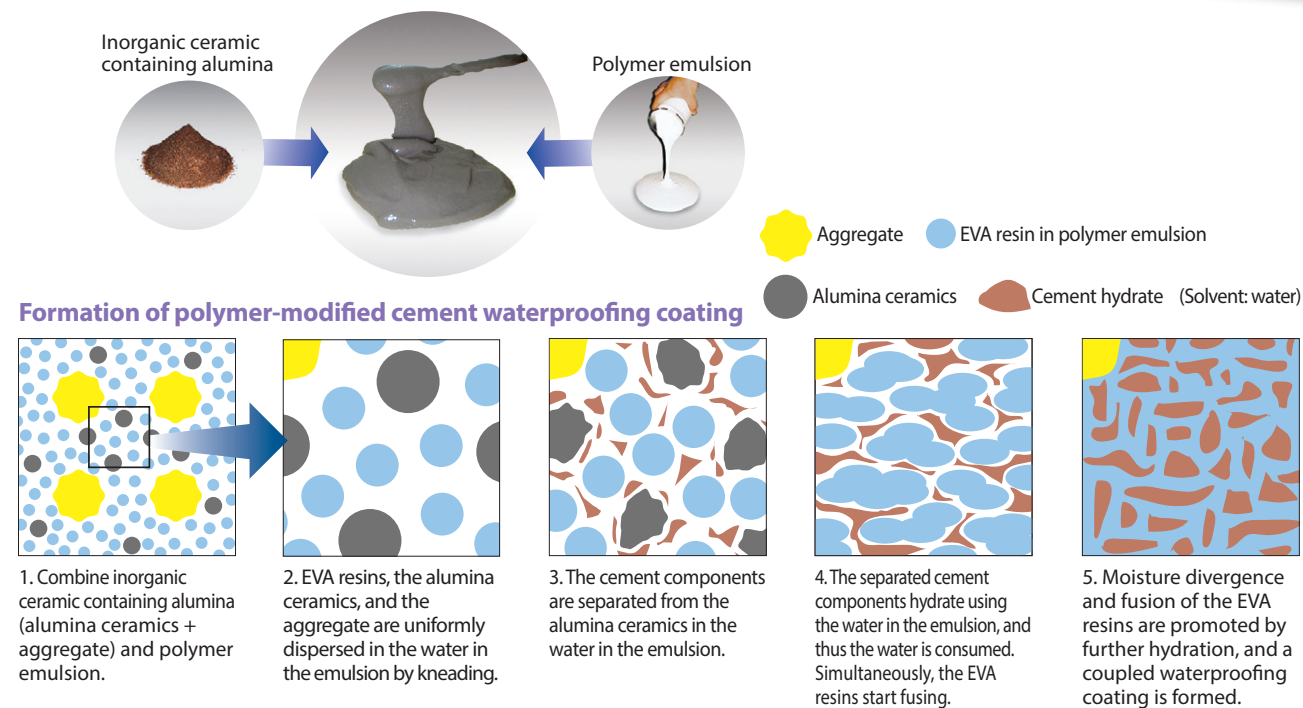
Pursuit of hydration and hardening processes

Achievements

- Observing the **cement hydration in polymer-modified cement waterproofing coating materials*** over time to clarify the process of cement hydrate production
- Realizing precise design method for materials suitable for each temperature and humidity in a construction environment to improve the reliability of products
- Adoption of the products in major facilities in Japan and overseas because of their improved performance and reliability (Examples of adoption: Roppongi Hills, Shanghai World Financial Center, Tokyo Urban Planning Group's Nerima Tunnel, etc.)

R&D facility: Ozeki Chemical Industry Co., Ltd.

***Polymer-modified cement waterproofing coating material:** A kind of waterproofing material used in construction and engineering work. When a polymer emulsion and cement admixture powder are mixed and kneaded at a construction site and applied to a base, the cement is hydrated to form a waterproofing coating. Polymer-modified cement waterproofing coatings are widely used as reliable and safe waterproofing materials because they combine the flexibility of polymers and the toughness and adhesiveness of cement and because they do not require the use of an organic solvent or open flame.



X-ray diffraction/
scattering

Role of SPring-8

Background

Polymer-modified cement waterproofing coating materials must have characteristics that are suitable for a wide range of environments because they are used under various conditions, such as high temperature and high humidity. In order to obtain materials with desirable properties under all conditions, it is essential to understand the process of cement hydration in detail and design materials so that the properties of the final coating can be predicted.

However, molecular-level microscopic measurement is needed to clarify the hydration process. Such measurement was difficult with general-purpose X-ray devices.

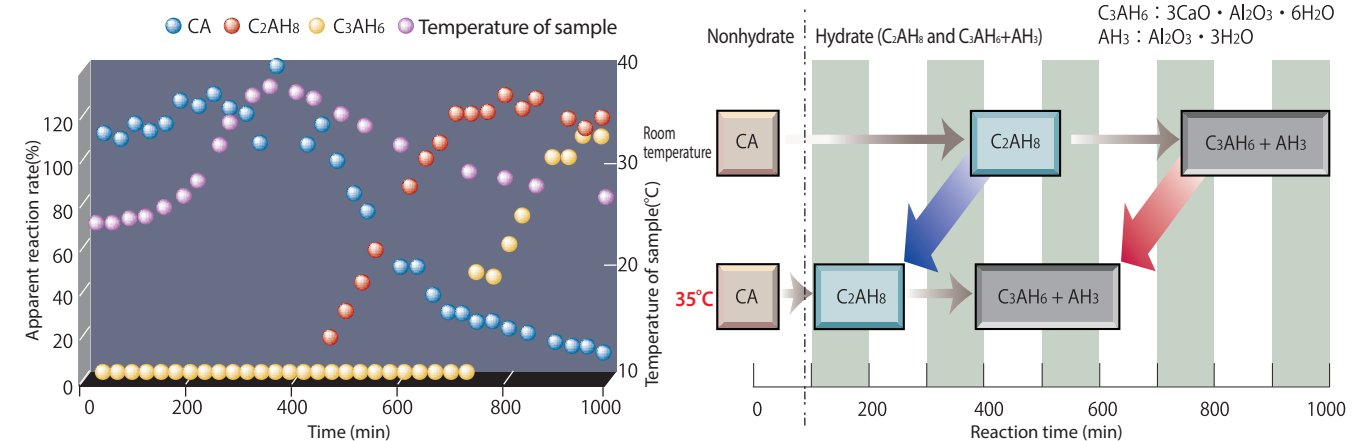
Results

We traced the entire hydration process in polymer-modified cement using high-brilliance X-ray diffraction in SPring-8, and examined when and how multiple cement hydrates are produced. In addition, we collected data using materials with the same combination ratio of cement and polymer emulsion by varying the temperature and humidity to quantitatively clarify the behavior of the materials, including changes in the reaction rate.

From these results, we made it possible to design materials that form a waterproofing coating even in a closed underground environment with a humidity of 100% by effectively using the water in the polymer emulsion to hydrate the cement.

Publication: M. Kotera et al.; Journal of The Society of Materials Science, Japan **54** (7), 780-784 (2005)

Progress of cement hydration measured in SPring-8 (at room temperature)



Development of Material Design Method for Autoclaved Lightweight Aerated Concrete

Analysis of formation mechanism of crystalline component tobermorite

Achievements

- Clarification of formation mechanism of crystalline component **tobermorite*** by in-situ observation of synthesis reaction of **autoclaved lightweight aerated concrete (ALC)****
- Paving the way for material design of ALC and control of its synthesis reaction

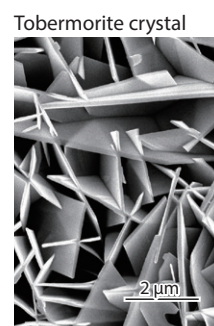
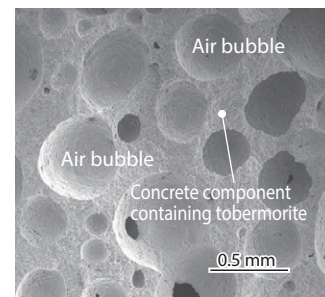
R&D facilities: Asahi Kasei Corporation and Asahi Kasei Construction Materials Corporation

***Tobermorite:** This is a crystalline calcium silicate hydrate, which forms the framework of ALC. It has high strength and durability in that it does not chemically change under heat or water. Tobermorite was first discovered in Tobermory (Scotland) in 1880 as a mineral, and it was named after the town. After that, the crystals existing in concrete produced under steam were found to be the same as those of the naturally occurring tobermorite.

****Autoclaved lightweight aerated concrete (ALC):** When a main material composed of silica, cement, and quick lime (calcium oxide) is mixed with water and a foaming agent (aluminum), the mixture foams and hardens similarly to a sponge cake and produces a porous concrete. The weight of ALC is one-fifth that of conventional concrete, and ALC has a high heat insulation and a high fire resistance. In Japan, ALC has become widespread since the 1960s as a building material. Nowadays, it is used for various purposes in many buildings as wall, floor, and partition materials.

Structure of ALC

In ALC, many air bubbles are dispersed and they are connected by fine pores. The air bubbles and fine pores comprise 80% of the total volume. Because ALC contains much air, similar to a down jacket, it has a high heat insulation capability. Tobermorite crystals grow at the surface of the air bubbles and fine pores.

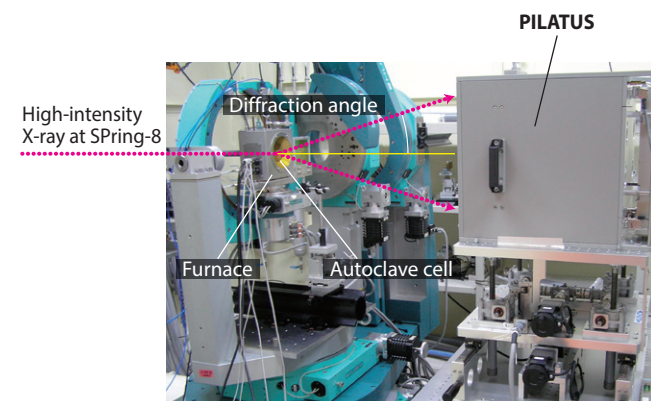


X-ray diffraction experiment at SPring-8

Two-dimensional pixel detector, PILATUS

PILATUS measures the X-rays diffracted by the material produced in the autoclave cell with a high time resolution.

PILATUS is a highly sensitive two-dimensional X-ray detector jointly developed by the Japan Synchrotron Radiation Research Institute (JASRI) and the Paul Scherrer Institute (PSI) in Switzerland.



Role of SPring-8

Background

The quality and quantity of tobermorite crystals determine the strength and durability of ALC. To grow platelike large crystals, the heat and water should be uniformly distributed in the material, and a condition under which the many air bubbles are generated as a space for crystal growth is necessary. To this end, ALC as a building material is produced using a high-temperature and high-pressure steam sterilizer (autoclave).

Recently, significantly increased performance of ALC has been demanded. However, as the chemical reaction occurring in the autoclave cannot be observed from the outside, changing the mixing ratio of the raw materials and synthesis conditions through trial-and-error was the only method adopted to improve the performance of the ALC.

Results

An autoclave cell was placed in the experimental hutch of a SPring-8 beamline. By irradiating the high-intensity X-rays on the material produced in the autoclave cell, the diffraction angle was measured to examine the contents of the synthesized material.

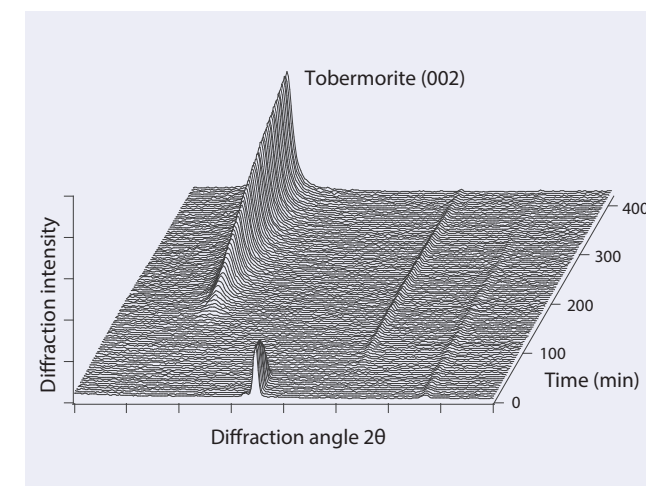
From the above examination, the formation mechanism of the tobermorite has been gradually revealed. It was considered that tobermorite was generated from calcium silicate hydrate (CSH) synthesized as a result of the reaction between silica and quick lime. In addition to this process, the existence of a route for generating tobermorite from monosulfate, a sulfate compound, via hydroxyl ellestadite (HE) was clarified. Furthermore, the timing at which the raw materials change into tobermorite was determined.

It became possible to proceed with the material design of ALC using the results obtained in this study as a guideline.

Publication: J. Kikuma et al.; Journal of Synchrotron Radiation **16**, 683-686 (2009)

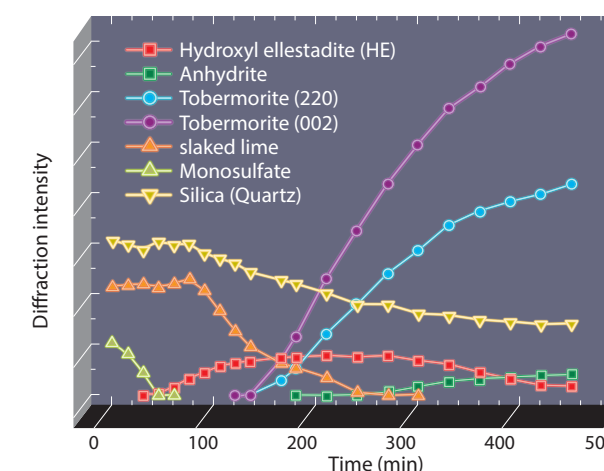
X-ray diffraction pattern observed in formation reaction of ALC

The X-rays diffract upon irradiation on a sample product. Each material has a unique diffraction angle, which can be used for identification. By observing the X-ray diffraction pattern, it is possible to identify when tobermorite is generated.



Change in mineral phase in formation reaction of ALC

As the amounts of silica and slaked lime (calcium hydroxide) decrease, more tobermorite is generated. This finding supports the CSH synthesis route, which is known conventionally. In addition, the existence of an intermediate product called monosulfate was revealed. A route in which the monosulfate disappears in an intermediate stage and tobermorite is then synthesized through hydroxyl ellestadite (HE), was found.



Responding to the Restriction of Hazardous Substances in Electronic Products

Establishment of high-sensitivity nondestructive inspection method for hexavalent chromium

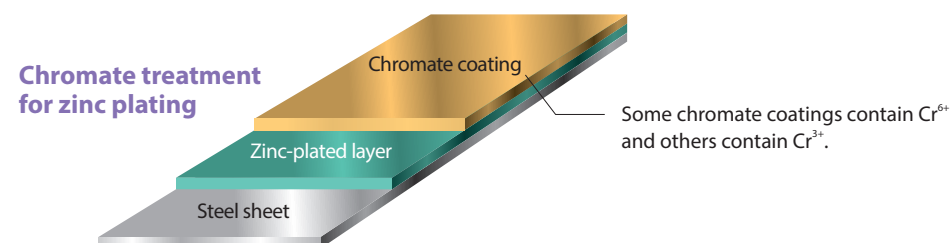
Achievements

- Development of a high-sensitivity nondestructive method for measuring the amount of hazardous **hexavalent chromium** in **chromate coatings*** used for protecting electronic products from corrosion
- Realization of a high-reliability rapid measurement method replacing the conventional inspection method involving melting
- Application of the developed method to satisfy the regulations imposed by the EU (**RoHS directive**)**

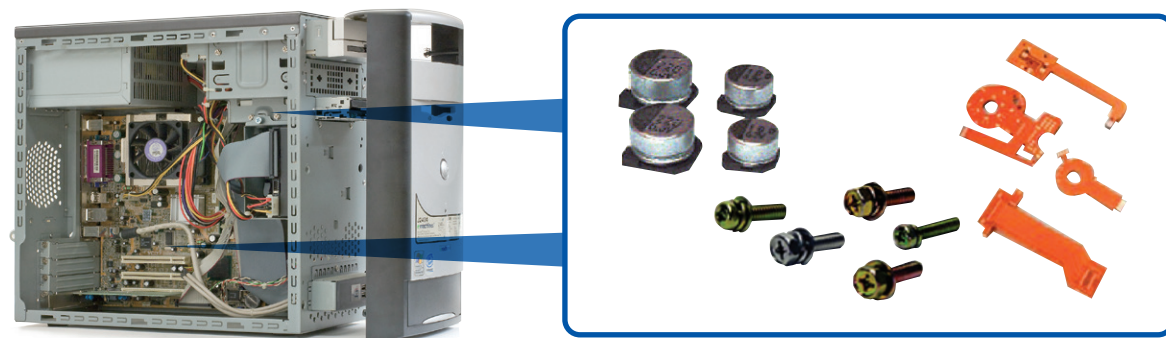
R&D facility: Fujitsu Laboratories, Ltd.

***Chromate coatings** are used for protecting iron and aluminum from corrosion. Some contain hexavalent chromium (Cr^{6+}) and others contain trivalent chromium (Cr^{3+}). Chromate coatings containing Cr^{6+} include yellow and black chromates and iridite. Cr^{6+} is a hazardous substance and causes diseases such as skin ulcers, nasal septum perforation, and lung cancer, and hence, the use of Cr^{6+} has started to be regulated. Cr^{3+} , less hazardous to human bodies than Cr^{6+} , has been studied for use in chromate coatings instead of Cr^{6+} .

****Restriction of Hazardous Substances (RoHS) directive**: a standard established by the European Union (EU) to regulate the use of specified hazardous substances in electric/electronic products, enforced in July 2006. The sale of products that do not conform to the RoHS directive is banned in the EU. Cr^{6+} is included in the list of regulated substances.



Iron and aluminum in electronic components are given a corrosion-proof coating.



Role of SPRing-8

Background

Measures to abolish the use of Cr^{6+} are being increasingly carried out because of the damage to human bodies caused by Cr^{6+} contained in electronic products and the environmental pollution due to the disposal of electronic products. Yet there has been no substantially reliable method of measuring the amount of Cr^{6+} through chemical treatment. What we need is a **nondestructive analytical method of detecting Cr^{6+}** .

In the method of analyzing Cr^{6+} through chemical treatment, Cr^{6+} is extracted by dissolving a chromate coating in unheated or hot water. In line with this, the following problems occur. The valency of Cr^{6+} changes during extraction, Cr^{6+} reacts with coexisting elements, and precise analysis is difficult for insoluble coatings. These result in unsatisfactory reliability.

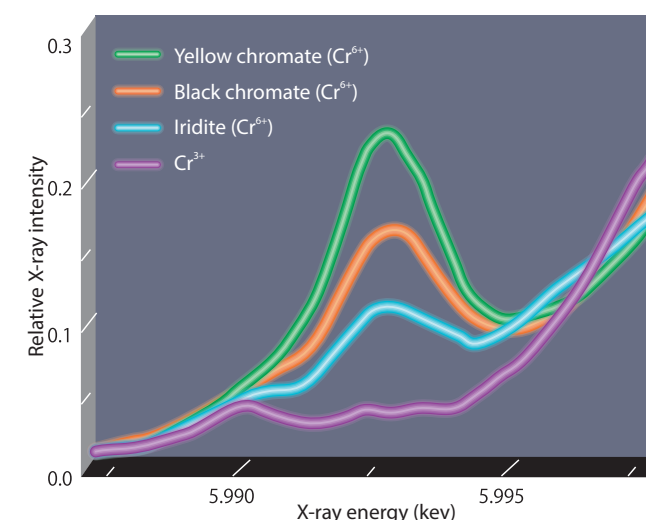
Results

The SPRing-8 XAFS method is appropriate for nondestructively measuring the absolute amounts of trace elements contained in samples. When Cr compounds were measured by the XAFS method, Cr^{6+} and Cr^{3+} were observed to be clearly separated in the absorption spectra. We measured and clarified the **absolute amount of Cr^{6+} (content rate)** for various chromate coatings by the XAFS method.

Moreover, it has become possible to obtain the depth distribution of Cr^{6+} in chromate coatings from the dependence of X-ray injection angle in the XAFS result. Thus, the technology for directly analyzing Cr^{6+} in chromate coatings without chemical treatment was improved.

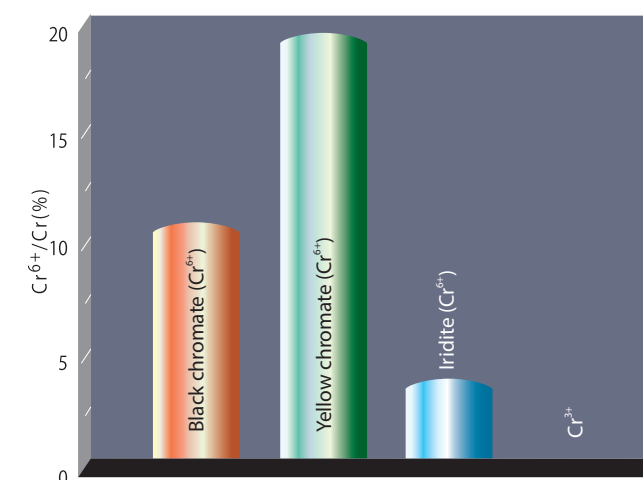
Measurement result for chromate by XAFS

The peak at 5.993 keV in the absorption spectrum for each chromate corresponds to Cr^{6+} . No peak is observed for Cr^{3+} . Thus, the content rate of Cr^{6+} can be measured.



Content rate of Cr^{6+} in each chromate

The content rate of Cr^{6+} is calculated from the XAFS spectra in the figure to the left.



Development of High-Efficiency Recycling Technology for Tungsten

Chemical state analysis of tungsten during ion exchange in collection system

Achievements

- Development of a method of collecting **tungsten*** using an **ion exchange method****
- Analysis of the change in the chemical state of tungsten during ion exchange
- Optimization of adsorption and elution conditions to enable the highly efficient collection of tungsten throughout the entire process (95%) and to reduce energy consumption by 40%

R&D facility: Sumitomo Electric Industries, Ltd.

† This research was supported by Japan Oil, Gas and Metals National Corporation (JOGMEC).

***Tungsten** is a rare metal with the chemical symbol W and the highest melting point of all metals. Tungsten production is small, and its extraction is locally distributed in China. Tungsten carbide is used as the principal component of carbide tools because of its high hardness.

****Ion exchange method:** A sample is placed in a column filled with an ion exchange resin, and the target substance is adsorbed onto the resin. Then, a buffer solution used for elution is introduced into the column to separate the adsorbed substance from the resin and obtain the target substance.

Used carbide tools and tips containing tungsten



Used carbide tips



Tools for urban development



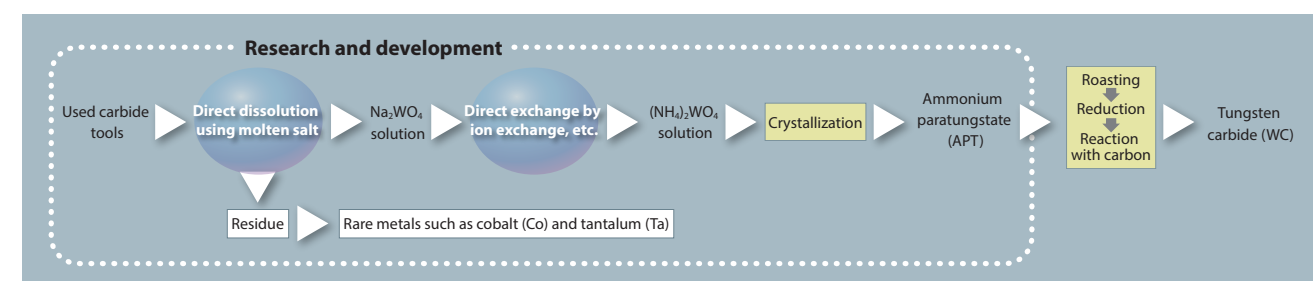
Used drills and endmills



Wear-resistant tools

Recycling process of tungsten

Used carbide tools are dissolved in molten salt to obtain a Na_2WO_4 solution. The solution is introduced into an ion exchange resin to collect tungsten ions in the $(\text{NH}_4)_2\text{WO}_4$ solution, which is then heated and condensed so that it crystallizes as ammonium paratungstate (APT). APT is oxidized by roasting to obtain WO_3 , which is then reduced to tungsten. The obtained tungsten is reacted with carbon to form the reusable tungsten carbide (WC).



Role of SPring-8

Background

Demand for tungsten is increasing, whereas its natural abundance is small. To help ensure a stable supply of tungsten, techniques for efficiently collecting and recycling tungsten from used carbide tools and tips are necessary.

Among the various methods for collecting tungsten, a method using an ion exchange column, which can be performed in a small-scale system compared with conventional methods, is expected to reduce the environmental load of tungsten recycling. To achieve efficient ion exchange, tungsten should be fully adsorbed onto an ion exchange resin and be completely eluted. In practice, however, tungsten crystals precipitate, clogging the column, and preventing the complete elution of tungsten. This has remained a long-standing problem.

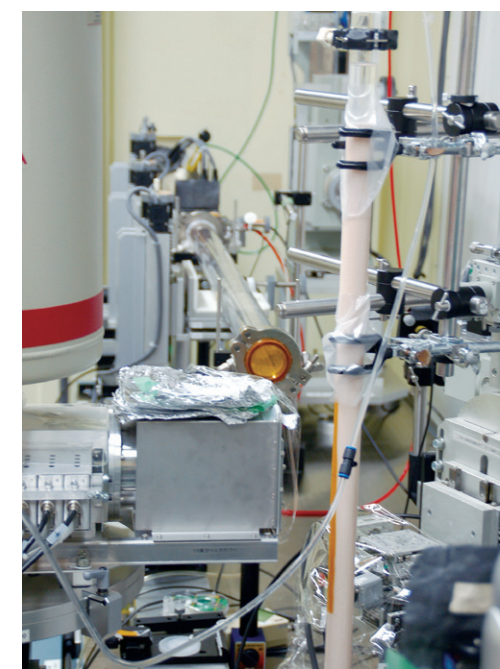
Results

X-ray absorption fine structure (XAFS) measurement using SPring-8 synchrotron radiation can reveal the electronic state and chemical structure of substances in a sample. Three tungsten ion species, WO_4^{2-} , $\text{HW}_6\text{O}_{21}^{5-}$, and $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$, were introduced separately into the ion exchange column, where they were adsorbed onto the ion exchange resin and eluted. XAFS measurement revealed that some of the adsorbed $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$ ions, which contain the most tungsten atoms of the three species, still remained in the resin. Detailed analysis clarified that the ions were partly decomposed into the other two ion species and these three ion species remained in the resin at a certain proportion.

From the above result, optimal conditions for the adsorption and elution of tungsten were determined, thus improving the collection efficiency of tungsten.

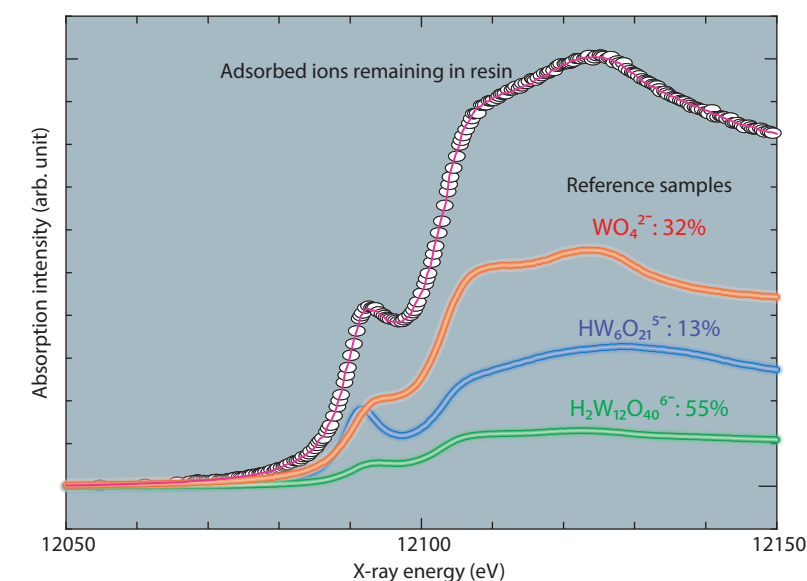
XAFS measurement at SPring-8

The long thin tube is the ion exchange column. Synchrotron radiation is irradiated onto the orange film.



XAFS measurement results for adsorbed ions remaining in resin during ion exchange of $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$

White circles represent measured values. The spectra of three tungsten ion species (WO_4^{2-} , orange; $\text{HW}_6\text{O}_{21}^{5-}$, blue; $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$, green) are used as references in the analysis. When the percentages of WO_4^{2-} , $\text{HW}_6\text{O}_{21}^{5-}$, and $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$ are 32, 13, and 55%, respectively, the spectrum of the adsorbed ions remaining in the resin fits the white circles. From this result, the percentages of the remaining ion species in the resin were obtained.



Development of Long-Life Next-Generation Li-Ion Batteries

Clarification of the causes of performance deterioration of Li-ion batteries

Achievements

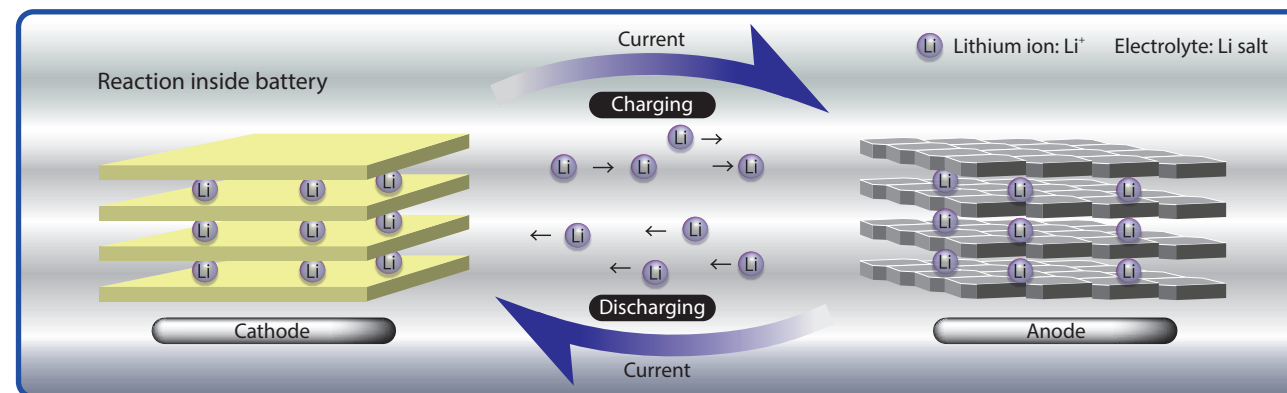
- Clarification of the causes of performance deterioration of next-generation **Li-ion batteries*** with a Ni oxide cathode at the atomic level by examining the charging and discharging processes
- Optimization of the composition of the cathode to suppress the **growth of the deteriorated layer** and to prolong the life of the batteries
- Paving the way to applying Li-ion batteries to hybrid and electric cars by the expected reduction of their weight and cost

R&D facility: Toyota Central R&D Labs., Inc.

***Li-ion battery:** a type of secondary battery that can be reused by charging. Li-ion batteries have been increasingly used in mobile electronic devices because of their lighter weight and greater capacity than Ni-Cd and Ni-MH batteries. Hybrid and electric cars also require long-life secondary batteries, and various R&D laboratories around the world are competing in the development of Li-ion batteries with improved performance.

Principle of Li-ion battery

A Li-ion battery comprises a cathode, an anode, an electrolyte, a separator, and other elements. The battery performance is determined by the cathode material, and LiCoO_2 is currently widely used. Graphite (C) is used for the anode and lithium salt for the electrolyte. During charging, the Li^+ in the cathode dissolve in the electrolyte and penetrate into the graphite structure of the anode. The opposite reaction occurs during discharging.



Role of SPring-8

Background

Li-ion batteries in practical use utilize Co as the cathode material. Only a small amount of Co is produced worldwide, and it is therefore expensive, which increases the cost of batteries. There is now a demand for next-generation batteries that use inexpensive abundant materials.

A material mainly composed of Ni oxide has recently attracted attention as a new cathode material to replace Co. However, this material has the problems that the structure of the cathode particles changes and the battery performance deteriorates at an early stage with repeated charging and discharging. The elucidation of the causes of these problems is desired.

Results

The SPring-8 high-brilliance X-ray enables us to directly observe the states of cathode particles. As a result of observing a battery that was repeatedly charged and discharged, it was clarified that a deteriorated layer with decreasing transmission of Li^+ was grown on the surface of the cathode particles and that Ni^{2+} block the path of Li^+ .

From the observation of batteries with different electrode compositions, we found a composition at which the formation of a deteriorated layer can be suppressed. Thus, the life of batteries was successfully prolonged.

Publication: T. Nonaka et al.; Journal of Electrochemical Society **154**, A353-A358 (2007)

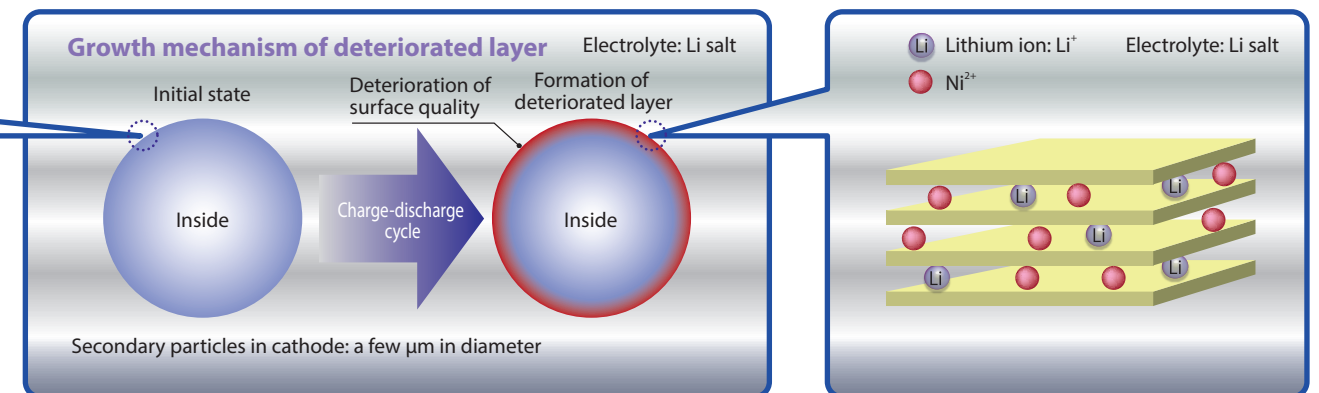
Mechanism underlying deterioration of battery performance

1) Growth of deteriorated layer

The actual cathode comprises cathode particles of a few μm diameter (secondary particles) surrounded by an electrolyte, each of which is an aggregate of a number of single-crystal particles (primary particles). It becomes increasingly difficult for the surface of these secondary particles to pass Li^+ upon repeated charging and discharging.

2) Deteriorated layer blocking path of Li^+

From the atomic-level observation, it was found that the path of Li^+ is blocked by Ni^{2+} that replace some of the Li^+ upon repeated charging and discharging.



Improvement of Capacity of Nickel-Metal Hydride Battery

Clarification of the optimal composition of the electrode

Achievements

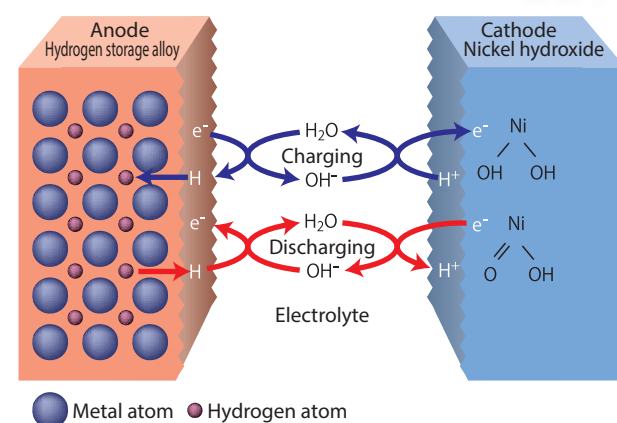
- Clarification of the relationship between the crystal structure of electrode materials used in **nickel-metal hydride batteries*** and changes in the discharge capacity with repeated charging and discharging
- Optimization of the composition of the alloys in the electrodes, and development of a product with at least 20% increased discharge capacity

R&D facility: GS Yuasa Corporation

***Nickel-metal hydride battery:** A type of secondary battery that can be reused after charging. This type of battery is characterized by the use of environmentally friendly hydrogen storage alloys (metal hydride that stores hydrogen atoms in the interstitial position of its crystals) without the use of lead or cadmium. Nickel-metal hydride batteries are used in various devices, such as cameras, PCs, and mobile phones, because their energy density is higher than that of Ni-Cd batteries.

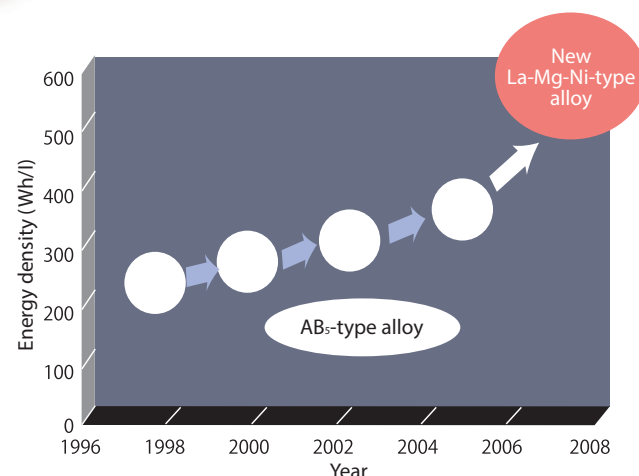
Principle of nickel-metal hydride battery

Nickel hydroxide and a hydrogen storage alloy are used as the cathode and anode, respectively. Hydrogen atoms move from the hydrogen storage alloy towards the nickel hydroxide cathode during discharging.



Change in energy density in AA-sized nickel-metal hydride battery

Battery performance depends on the quality of the hydrogen storage alloy used as the anode material, and its improvement has been promoted. The discharge capacity of a battery that uses a rare earth-nickel-based alloy (AB₅-type alloy) as the anode material is at least 85% of the theoretical value; therefore, the further improvement of the capacity is difficult.



Role of SPring-8

Background

The discharge capacity of nickel-metal hydride batteries depends on the reaction rate of hydrogen storage by the anode alloy and on the amount of hydrogen reversely released from the alloy (amount of hydrogen storage). Therefore, hydrogen storage alloys based on various new elements are being actively studied. In particular, **La-Mg-Ni-type alloys** are drawing much attention.

However, La-Mg-Ni-type alloys, which can store a very large amount of hydrogen, have a disadvantage in the sense that their performance deteriorates with repeated charging and discharging. To optimize their composition, it is necessary to clarify their crystal structure, but conventional methods were unsatisfactory to observe the crystal structure, which contains various stacking structural phases.

Results

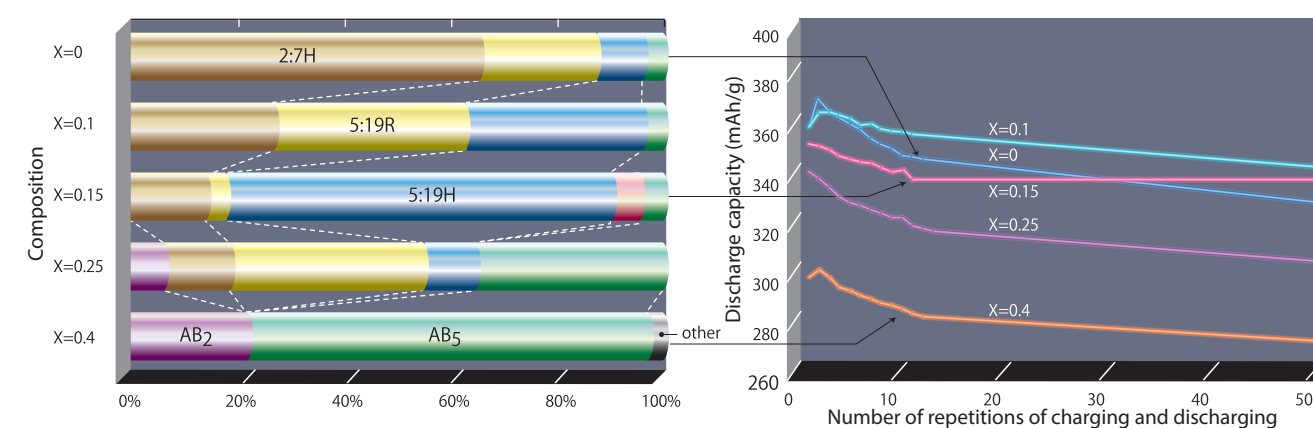
By observing La-Mg-Ni-type alloys by X-ray diffraction using the synchrotron radiation of SPring-8, it was clarified how the various crystal structures of the alloy, which contains various elements, change depending on the percentage of the metals added (manganese and aluminum). Moreover, we analyzed the discharge capacity and changes in the performance due to repeated charging and discharging for different crystal structures. We found the optimal crystal structure that can maintain high capacity in a stable manner from among the various possible phases.

From the above result, we successfully obtained guidelines for designing electrode materials.

Publication: T. Ozaki et al.; Journal of Alloys and Compounds **446-447**, 620-624 (2007) T. Ozaki et al.; ITE Letters **8**(4), B24 (2007)

Phase structure of La_{0.8}Mg_{0.2}Ni_{3.4-x}Co_{0.3}(MnAl)_x alloy

The crystal structures of alloys are dependent on the percentage of manganese and aluminum added, (MnAl)_x. In particular, at x=0.15, Mn and Al substitute specific Ni sites that are sandwiched between rare-earth elements, leading to the stabilization of a 5:19 phase.



Relationship between number of repetitions of charging and discharging and discharge capacity

The discharge capacity of the alloy that contains a large amount of the 5:19 phases (x=0.15) hardly decreases even with repeated charging and discharging. This is because the degree of expansion and contraction due to the absorption and release of hydrogen, respectively, is small in the 5:19 phase.

Establishment of Method for Analyzing Next-Generation Metal-Oxide-Semiconductor Field-Effect Transistors

Nondestructive analysis of internal states of semiconductor laminated structures

Achievements

- SPring-8 synchrotron radiation has improved the detection sensitivity for internal property of a material by approximately fivefold compared with conventional **X-ray photoelectron spectroscopy**.*
- For a laminated electrode/insulating-film/semiconductor structure, the relationship between the change in the photoelectron spectrum and the applied voltage has been clarified to calculate the voltage applied to the insulating film.
- An analysis technique that can be used to develop next-generation **metal-oxide-semiconductor field-effect transistors (MOSFETs)**** has been established.

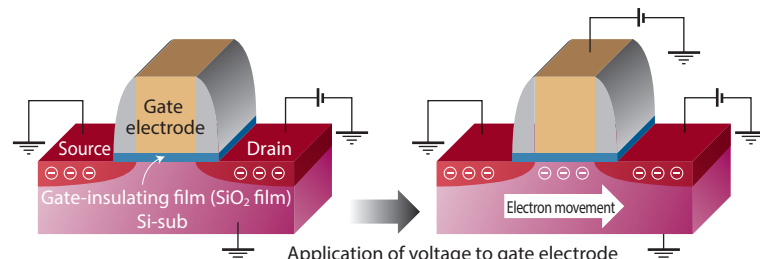
R&D facility: Toshiba Corporation

***X-ray photoelectron spectroscopy** is a method of analyzing the elements of a sample surface and their electronic states by measuring the energy of photoelectrons emitted upon X-ray irradiation of the sample. The depth to which the sample can be analyzed depends on the energy of the irradiated X-rays. In laboratories, soft X-rays such as Al-K α (1.4867 keV) are used. In contrast, at SPring-8, synchrotron radiation hard X-rays with an energy of 4-10 keV are used, enabling the analysis of samples at a greater depth. This method of using hard X-rays is called **hard X-ray photoelectron spectroscopy (HAXPES)**. Most of the measurement and analysis techniques used for soft X-ray photoelectron spectroscopy and HAXPES are the same; only the energy of the X-rays is different.

A **metal-oxide-semiconductor field-effect transistor (MOSFET) is a field-effect transistor that controls the current between the source and drain by applying different voltages to the gate electrode. A laminated structure consisting of a metal (as the gate electrode between the source and drain), an oxide (as a gate-insulating film), and a semiconductor (a silicon substrate) is adopted in a MOSFET. Many current large-scale integrated circuits (LSIs) adopt a MOSFET structure.

Structure and operation of MOSFET

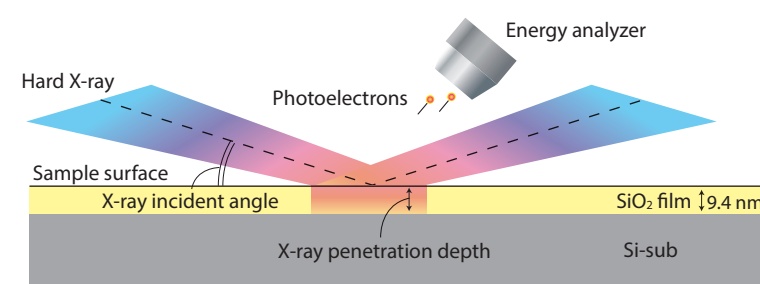
A MOSFET has a laminated structure in which a gate-insulating film is sandwiched between a silicon substrate (Si-sub) and a gate electrode. Silicon dioxide (SiO₂) is generally used for the gate-insulating film. When a voltage is applied to the gate electrode, carriers are generated immediately below the SiO₂ film to allow current to flow between the source and drain.



Total-reflection HAXPES

Total reflection is induced when X-rays are irradiated at a surface at a very small incident angle. Even in the case of total reflection, hard X-rays can penetrate into a sample to approximately several nanometers below the surface, thus efficiently exciting photoelectrons. The penetration depth can be varied by controlling the incident angle, meaning that the depth of the layer in which photoelectrons are excited can be changed.

To examine the increase in detection sensitivity and the change in penetration depth for the case of total reflection using HAXPES, a SiO₂ film was observed by this method.



Role of SPring-8

Background

With the aim of developing next-generation MOSFETs, the introduction of new devices, such as ferroelectric gate-insulating films and metal gate electrodes, and the fabrication of multilayered insulating films have been examined. Therefore, methods of analyzing such new materials and their inner structure should be established.

Conventionally, X-ray photoelectron spectroscopy has been used for such analysis; however, only the surface of a sample can be observed with this method, and the inner structure of a sample cannot be observed without physically destroying the sample. In addition, it may not be possible to analyze spectra because the number of observable photoelectron peaks is small and the peaks of the spectra corresponding to different coexisting elements may interfere with each other. In some cases, satisfactory accuracy cannot be obtained due to the complicated shape of the peak spectrum.

Photoelectron spectroscopy



Research method

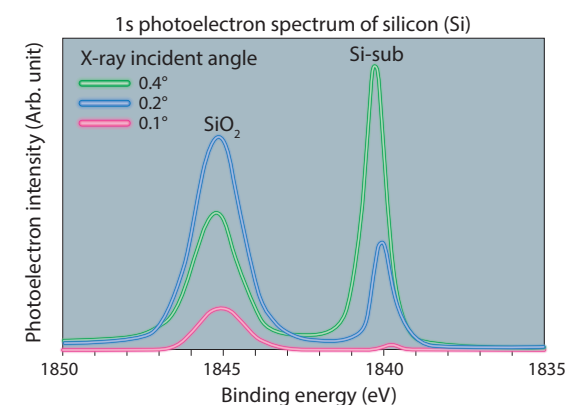
Results

In the case of HAXPES using intense SPring-8 synchrotron radiation, the depth of observation is as high as 20-30 nm and the number of observable photoelectron peaks is increased. Furthermore, optimum observation conditions were determined for the total reflection method, in which grazing incident X-rays are totally reflected on the sample surface, to obtain the distribution of elements in the depth direction by changing the observation depth with increased detection sensitivity.

In addition, the behavior of the photoelectron spectra was observed by changing the voltage in a stepwise manner to evaluate the potential distribution induced in the semiconductor laminated structure when a voltage is applied. The voltage applied to the insulating film was precisely determined. Using the results obtained, the development of next-generation MOSFETs is being carried out.

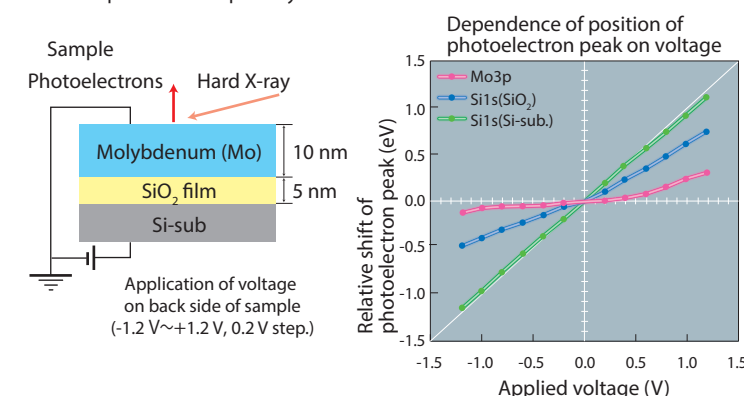
Observation results of photoelectron spectra under total-reflection condition

When the incident angle of hard X-rays is 0.4°, the intensity of the photoelectron peak corresponding to a SiO₂ film on the surface side is smaller than that corresponding to the Si-sub, whereas when the incident angle is 0.2°, the relative intensities are reversed. When the incident angle is 0.1°, the peak corresponding to the Si-sub is negligible. From this result, it was found that the smaller the incident angle, the shallower the depth of observation using X-rays.



Measurement of photoelectron spectra under voltage application

With HAXPES, the measurement of photoelectron spectra with a voltage applied to the electrode is possible because a sample with a thick laminated structure can be observed nondestructively. The positions of the photoelectron peaks corresponding to each laminated layer were measured while applying a voltage to the sample with a gate stack structure. The results indicate that the relative shift of the photoelectron peak of each layer depends on the applied voltage and that the voltage applied to the insulating film depends on the polarity.



Accurate Analysis of Molecular Orientation of Organic Semiconductor Material

Clarification of excellent electric properties of transistor devices fabricated by vacuum deposition

Achievements

- Successful fabrication of transistor device with high mobility by **vacuum deposition*** using 2-decyl-7-phenyl [1] benzothieno [3,2-b] [1] benzothiophene (Ph-BTBT-10), an organic semiconductor with excellent charge transport properties
- Demonstration of excellent charge transport properties (hole mobility, $>10 \text{ cm}^2/\text{Vs}$) by transistor device evaluation
- Confirmation of thin-film crystal structure (molecular arrangement) that gives Ph-BTBT-10 its high mobility by analysis of deposited thin film by **two-dimensional grazing incidence X-ray diffraction (2D-GIXD)****

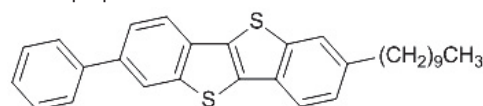
R&D Institution: Tokyo Chemical Industry Co., Ltd.

***Spin coating and vacuum deposition:** These are both typical methods for fabricating semiconductor thin films. In spin coating, a semiconductor solution is dropped onto a substrate, which is rotated (spun) at a high speed to coat its surface with the semiconductor. In vacuum deposition, a thin film of a material is formed by vaporizing (evaporating) the material in vacuum, and the vaporized material is deposited on the surface of a substrate.

****2D-GIXD:** When a sample surface is irradiated with an X-ray beam nearly parallel to the surface, faint diffraction signals can be obtained from a thin film layer. This is called grazing incidence X-ray diffraction (GIXD). When the signals are detected two-dimensionally, the preferred orientation of the sample can be evaluated. This is called 2D-GIXD.

Ph-BTBT-10

Ph-BTBT-10 (upper) is a commercially available (lower) p-type organic semiconductor material with excellent transistor properties.

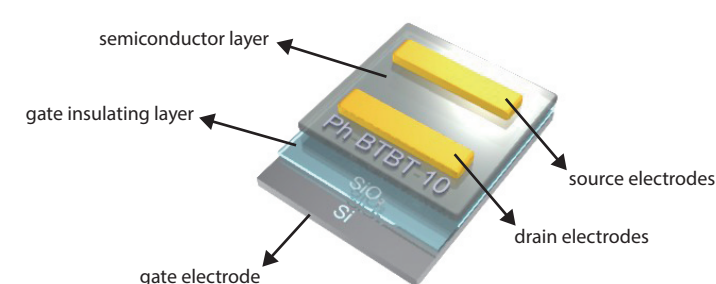


OFET device performance

Stable p-type semiconductor characteristics were observed for the transistor device fabricated by depositing a Ph-BTBT-10 thin film (right table). By annealing the deposited thin film, the transistor performance was greatly improved, that is, a maximum hole mobility of $\mu_{\text{max}} = 14.0 \text{ cm}^2/\text{Vs}$ was achieved for the octadecyltrichlorosilane (ODTS)-treated substrate.

OFET device fabricated using Ph-BTBT-10

A Ph-BTBT-10 thin film was formed on a silicon wafer ($\text{n}^+\text{-Si}/\text{SiO}_2$). A gold (Au) layer was deposited on the thin film. Silicon ($\text{n}^+\text{-Si}$), silicon dioxide (SiO_2), Ph-BTBT-10, and Au were used as the gate electrode, gate insulating layer, semiconductor layer, and source/drain electrodes, respectively.



Fabrication Method	Substrate	Annealing Temp. (°C)	Mobility (cm^2/Vs)	Vth (V)
Vacuum Deposition	Bare	w/o	0.87 ~ 0.91	-24
	(Si/SiO ₂)	120	4.24 ~ 4.86	-8
	ODTS (Si/SiO ₂ /ODTS)	120	10.3 ~ 14.0	-22

Role of SPring-8

Background

Organic semiconductors are lightweight and flexible. Focusing on these advantages, the research and development of organic field-effect transistors (OFETs) have been intensively carried out towards their application in next-generation devices, such as stretchable and bendable electronic circuits and medical sensors that can be attached to the skin.

Ph-BTBT-10 is a liquid crystalline organic semiconductor that is soluble in common organic solvents and has high thermal durability, film formability, and air stability. In a previous study, it was found that an OFET device fabricated using Ph-BTBT-10 by spin coating showed a high hole mobility ($>10 \text{ cm}^2/\text{Vs}$).¹⁾ In this study, it was also found that a comparable mobility was obtained for a device fabricated by vacuum deposition. To determine the reasons for the excellent electric properties, it was necessary to reveal the thin-film crystal structure (molecular arrangement) in the vacuum-deposited thin film of the organic semiconductor using crystallography techniques.

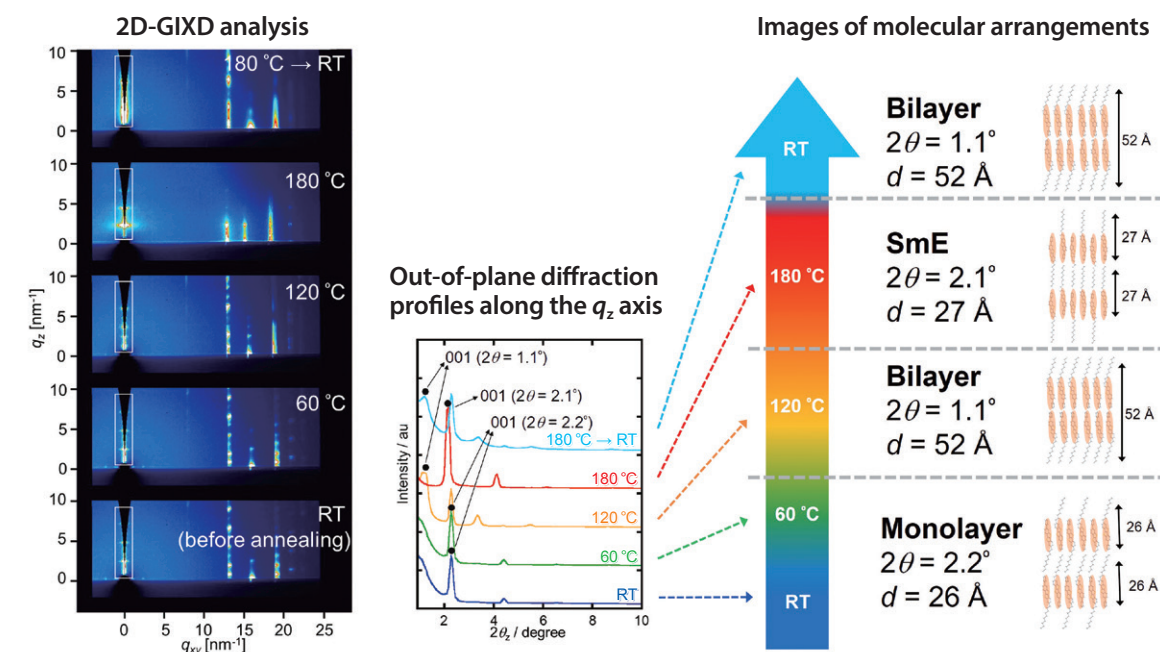
Results

An OFET device using Ph-BTBT-10 was fabricated by vacuum deposition and its transistor characteristics were evaluated. The results revealed that Ph-BTBT-10 was not thermally decomposed and its electrical properties were not deteriorated during the vacuum deposition process. The device fabricated by vacuum deposition showed excellent electric charge transport characteristics (hole mobility, $>10 \text{ cm}^2/\text{Vs}$) comparable to those of a device fabricated by spin coating.

The molecular arrangement of the deposited thin film was analyzed by 2D-GIXD at SPring-8. The X-ray obtained from SPring-8 beamlines has an intensity much higher than that of general X-ray diffraction systems and enables the fast and accurate analysis of the molecular arrangement of organic thin films. The analysis results suggest that the crystal structure (molecular arrangement) of the vacuum deposited thin film was the same as that of the spin-coated thin film, verifying the high mobility of the device fabricated by vacuum deposition.

Results of 2D-GIXD analysis

The interlayer distance in the out-of-plane direction was calculated from the diffraction peaks along the q_z -axis (indicated by white boxes). The molecular arrangement of Ph-BTBT-10 in the deposited thin film was predicted at each substrate temperature. The obtained diffraction peaks suggest that the crystal structure (molecular arrangement) of the post-annealed deposited thin film was the same as that of the spin-coated thin film.¹⁾



Reference H. Iino, T. Usui, J. Hanna, *Nat. Commun.* 2015, 6, 6828.

Research and Development of Stainless Steel with Hydrogen Embrittlement Resistance

Analysis of crystalline phase causing hydrogen embrittlement

Achievements

- Demonstration of the existence of a phase causing **hydrogen embrittlement**** by observing the crystalline microstructure of **stainless steel*** at room temperature
- Contribution to the research and development of a stainless steel resistant to hydrogen embrittlement and its applications

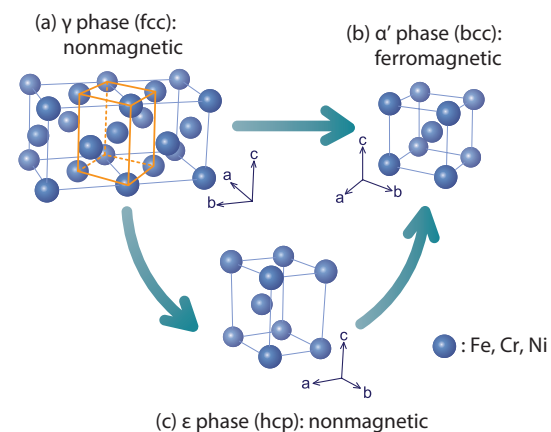
R&D facility: NIPPON STEEL Stainless Steel Corporation and Osaka Prefecture University

***Stainless steel:** Stainless steel is an iron alloy containing a minimum of 11% Cr. About ~ 50 million tons of stainless steel is produced worldwide per year. SUS304 (18-8 stainless steel) is a typical stainless steel that contains 18% Cr and 8% Ni and has high strength, ductility, and corrosion resistance. Therefore, it has been widely used as a material in built-in kitchens, elevators, and chemical plants and tanks.

****Hydrogen embrittlement:** Hydrogen embrittlement is a phenomenon that occurs in metals. When an external force is applied to metals into which hydrogen penetrates, their ductility and toughness decrease and they become brittle. Metals suffering from hydrogen embrittlement may break upon the application of force.

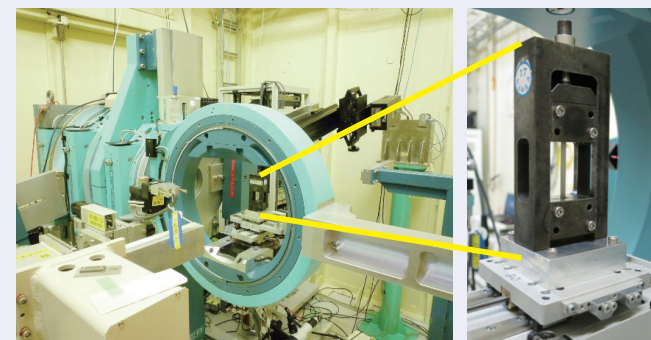
*****Lorentz transmission electron microscope (TEM):** A Lorentz transmission electron microscope is used to observe the magnetic domains of magnetic materials. Electrons that enter a ferromagnetic substance change their direction of travel upon the application of a Lorentz force via a magnetic field (deflection). Electrons are subjected to different deflections from neighboring magnetic domains. This enables a contrast to be observed at the neighboring magnetic domains in images, revealing the boundary of the phases.

Change in crystalline microstructure of SUS304



SUS304 crystals are nonmagnetic and have the face-centered-cubic crystalline structure (γ phase). When a SUS304 specimen is strained at room temperature, the γ phase is transformed to the body-centered-cubic crystalline microstructure (α' phase) and the specimen becomes ferromagnetic (deformation-induced martensite transformation). This transformation improves the strength and ductility of SUS304. In this study, the generation of the ϵ phase, which is considered to cause hydrogen embrittlement, was confirmed during the transformation process from the γ phase to the α' phase.

X-ray diffraction experiment at SPring-8



A multiaxis diffractometer, which enables easy control of the incident angle of X-rays and the detection angle of diffracted X-rays, and a tensile testing machine were installed in the station of BL02B1. The *in situ* observation of stretched SUS304 specimens with and without prestrain was carried out.

Role of SPring-8

Background

In addition to the use of renewable energy as an alternative to fossil fuels, hydrogen has been attracting much attention as a source of energy. Stainless steel is a promising material for containers used for the storage and transport of hydrogen because of its excellent mechanical properties such as high strength and ductility as well as corrosion resistance. However, it may undergo hydrogen embrittlement.

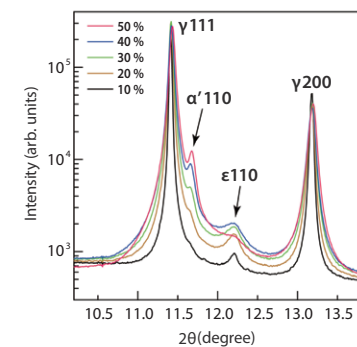
To develop stainless steel with hydrogen embrittlement resistance, the mechanism underlying hydrogen embrittlement should be clarified. However, the theory of hydrogen embrittlement has not been explained, and it has been difficult to observe the change in the crystalline microstructure during the processing of stainless steel at room temperature at an atomic scale.

Results

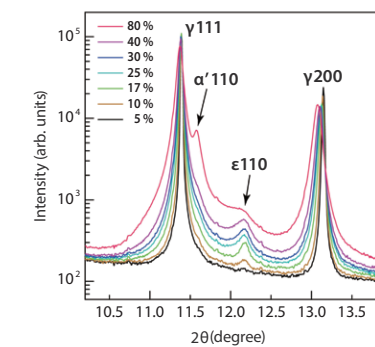
In situ X-ray diffraction observation of SUS304 specimens with and without prestrain was carried out at SPring-8 while the specimens were strained using a tensile testing machine. The results indicate that the ϵ phase, which is considered to be the cause of hydrogen embrittlement, was observed when the crystalline microstructure of the specimen transformed from the nonmagnetic γ phase to the ferromagnetic α' phase. In addition, the site where the crystalline phase was formed was observed using a **Lorentz transmission electron microscope*****. The ϵ phase was observed at the twin boundary between the nonmagnetic γ phase or ϵ phase and the ferromagnetic α' phase.

The above results indicate the existence of the ϵ phase, which is considered to cause the hydrogen embrittlement of stainless steel at room temperature, but it has not been observed thus far. It is expected that a new stainless steel with hydrogen embrittlement resistance will be developed and that new applications of this stainless steel will be proposed in the future.

Observation of X-ray diffraction profiles using SUS304 specimens with and without prestrain

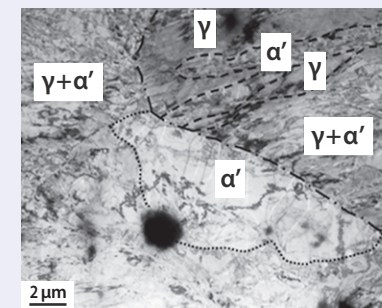


With increasing amount of tensile strain (10%, 20%,...), the area of the peak of the ϵ phase in the profile increases up to a tensile strain of 40%, after which it decreases. From this result, it is found that the ϵ phase starts to transform to the ferromagnetic α' phase at a tensile strain of ~ 30%.

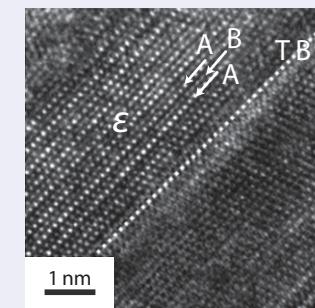


To observe the transformation process from the ϵ phase to the α' phase, *in situ* observation of strained SUS304 specimens without tensile strain was carried out. With increasing amount of strain, the amount of the ϵ phase increases, which is followed by the appearance of the α' phase.

Observation of magnetic phase: Lorentz TEM image of fracture specimen



The boundary between black and white magnetic phases was observed in the area of the α' phase in a Lorentz TEM image of a fractured specimen.



An array of crystals unique to the ϵ phase ("ABAB") was observed in the high-resolution TEM image of a SUS304 specimen subjected to 20% tensile strain (compared with "ABC" in the general γ phase).

Establishment of Laser Peening Technology for Improving Surface Quality of Metallic Products

Optimization of laser irradiation conditions to enhance the effect of surface-quality improvement

Achievements

- Establishment of optimal laser irradiation conditions for **laser peening*** to improve the surface quality by measuring the depth profiles of **residual stress**** on a metal surface nondestructively
- Confirming the suppression of the fatigue-crack growth on metals by laser peening through 3D imaging of the cracks
- Establishment of laser peening technology for suppressing the initiation and development of cracks in the nuclear-reactor structures

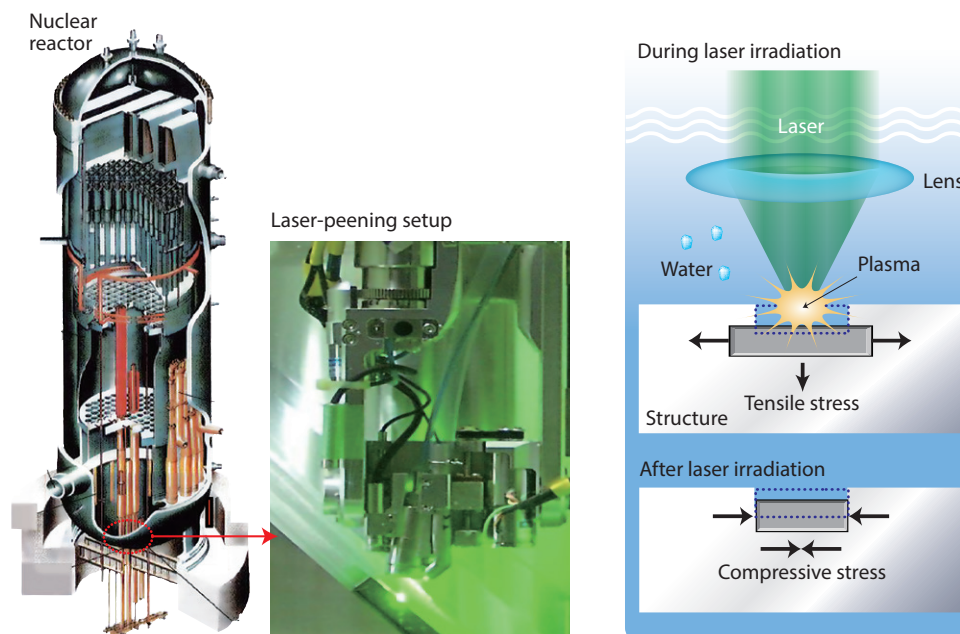
R&D facility: Toshiba Corporation

***Laser peening:** Peening is similar to the hammering process used by a swordsmith. Compressive residual stress is imparted to a metal surface by peening to cancel the tensile stress inside the metal, changing it into compressive stress. Hence, the prevention of fatigue and stress corrosion cracks from developing in welded parts is realized. In laser peening, a metal surface is compressed by the shock of plasma (high-pressure gas) that is generated by irradiating an intense pulsed laser onto the metal surface, and introduces compressive residual stress inside the metal. Laser peening technology has been used for nuclear reactors and is considered for application to the components of airplanes, automobiles, and bridges.

****Residual stress:** Stress retained inside an object even after the removal of the external forces such as tension, compression, bending, and heat treatment.

Principle of laser peening

The surface layer of a metal in water changes into plasma upon the irradiation of a high-intensity pulsed laser. Because plasma expansion is prevented in water, the laser energy becomes locally concentrated on the metal surface, generating shock waves. The metal surface is slightly deformed by these shock waves; however, its further deformation is hampered by the surrounding parts. Thus, the material is strengthened by the compressive stress remaining on its surface.



Role of SPring-8

Background

Shot peening with fine metallic balls being shot at materials is a well-known peening technology. However, this method is not suitable for peening in some cases, such as the inside of nuclear reactors, because of its large-scale setup and the difficulty in retrieving the metallic balls. There has been demand for a new peening technology with a compact setup.

With this background, laser peening using a high-intensity pulsed laser has come into the spotlight. However, it is difficult to observe the interior and fine regions of materials and measure the residual stress on sites very close to the surface using a conventional X-ray.

Results

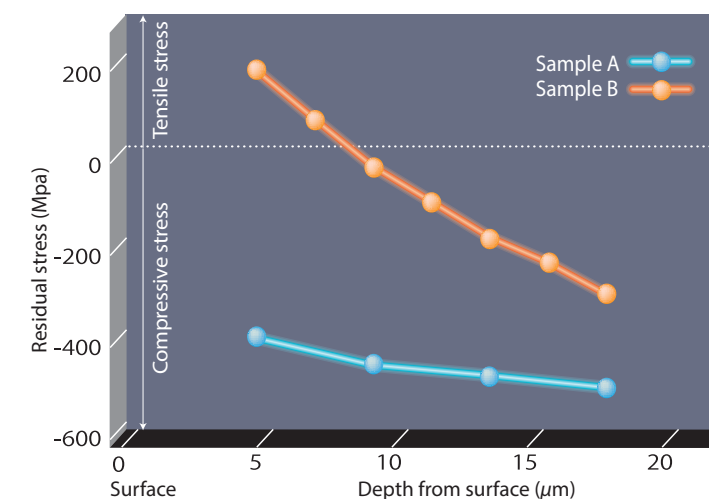
The synchrotron radiation X-ray of SPring-8 has a high transmittance, enabling us to nondestructively measure the states of materials processed by laser peening from their surface to their interior. We demonstrated that the residual tensile stress on the surface and interior is changed into compressive stress by laser irradiation. Moreover, the **depth profiles of residual stress** were compared between different laser irradiation conditions to determine the optimal conditions.

In addition, the images obtained from X-ray computerized tomography (CT) clearly revealed that the **growth of fatigue cracks** was markedly suppressed for materials processed by laser peening.

Publication: Y. Sano and K. Akita; SPring-8 Research Frontiers 2005, 127-128 (2006) Y. Sano and K. Masaki; SPring-8 Research Frontiers 2006, 151-152 (2007) K. Masaki et al.; Journal of Solid Mechanics and Materials Engineering 2 (8), 1104-1113 (2008)

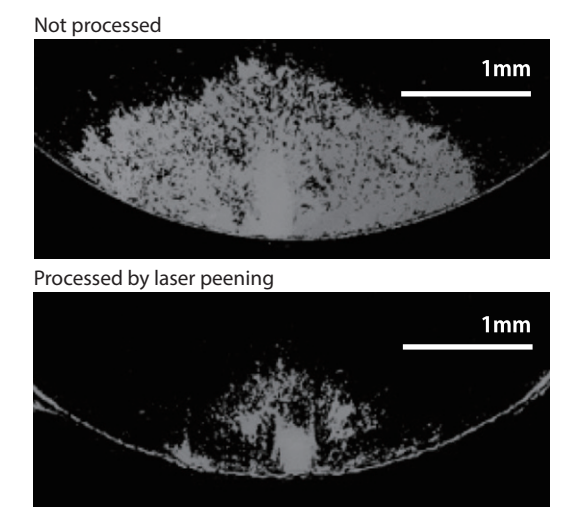
Depth profile of residual stress

Tensile stress remains on the surface of sample B after the sparse laser irradiation to the target surface. Sufficient compressive stress is applied to the surface and inside of sample A after dense laser irradiation to the target surface.



X-ray CT image of fatigue crack generated on aluminum alloy

The growth of fatigue cracks (the white parts in the center) is suppressed on the specimen processed by laser peening.



Suppression of Solidification Crack upon Steel Welding

The world's first successful Two-dimensional Time-resolved X-ray diffraction of metallographic changes in weld metals during real welding at a resolution of 0.01 sec.

Achievements

- Paving the way to suppression of **welding solidification crack*** in weld metal by detailed measurement of metallographic changes of **high-alloy steel**** weld metal in the melting and solidification processes during welding

R&D facility: Sumitomo Metal Industries, Ltd., Osaka University, and Japan Synchrotron Radiation Research Institute

***Welding solidification crack:** Welding involves the rapid melting and solidification of weld metal. A membrane (liquid phase) with a low melting point is formed during welding, and stress due to its contraction acts on the membrane while solidifying, causing a network of cracks. This is known as welding solidification crack.

****High-alloy steel:** The percentage of alloy elements added to steel is at least 10%.

Role of SPring-8

Background

The prevention of welding solidification crack is essential for improving the reliability of materials at the welded part. For this purpose, a reduction of metals causing a decrease in the solidification temperature at the welded part has been tried; however, a number of difficulties remain for practical application.

To prevent solidification crack, it is necessary to examine the welding solidification process in detail, clarify the mechanism behind the formation of solidification crack, such as when and what substances are produced, and predict the formation of solidification crack.

Results

For the in situ observation of metallographic changes at the welded part, we used our actual welding machine and applied PILATUS,* a two-dimensional pixel detector to catch weak signals. As a result, we succeeded in two-dimensional capturing the **metallographic changes during rapid cooling over 100 K/s**, and in establishing guidelines for material design to prevent solidification crack.

For example, niobium forms a carbide earlier as the amounts of niobium and carbon in an alloy are increased. The importance of the timely and stable formation of niobium carbide was clarified to prevent solidification crack.

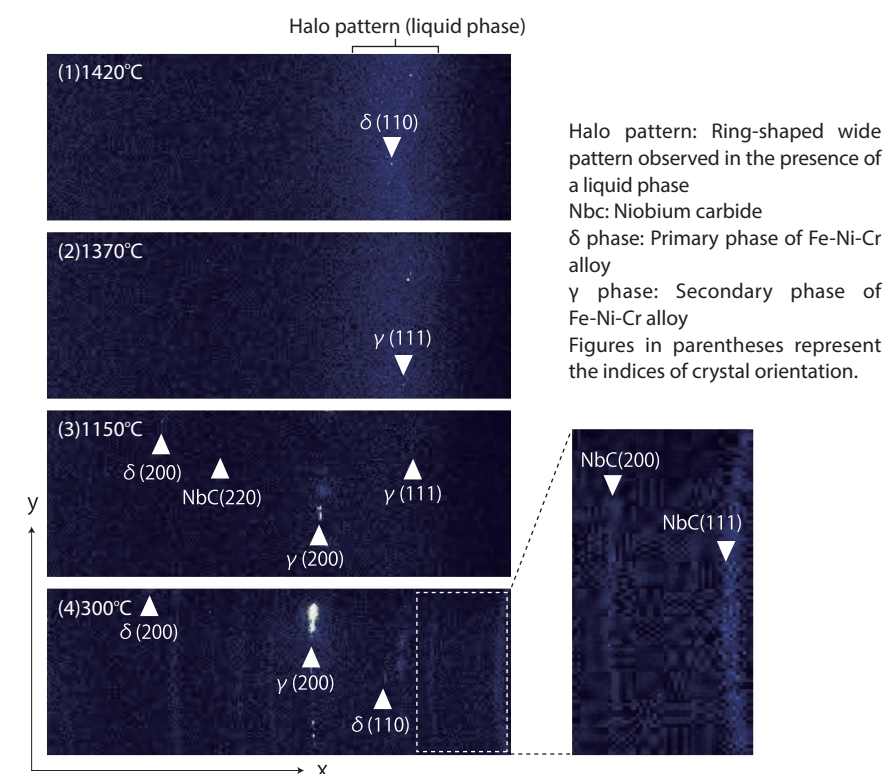
*PILATUS: High-sensitivity high-speed two-dimensional X-ray detector developed in a collaboration between Japan Synchrotron Radiation Research Institute and Paul Scherrer Institut (PSI) in Switzerland.

Publication: M. Yonemura et al.; Materials Transactions **47**, 2292-2298 (2006) Y. Komizo et al.; Quarterly journal of the Japan welding society **24**, 57-64 (2006)
M. Yonemura et al.; Tetsu-to-Hagane **93**, 68-74 (2007)

X-ray diffraction pattern for high-alloy steel

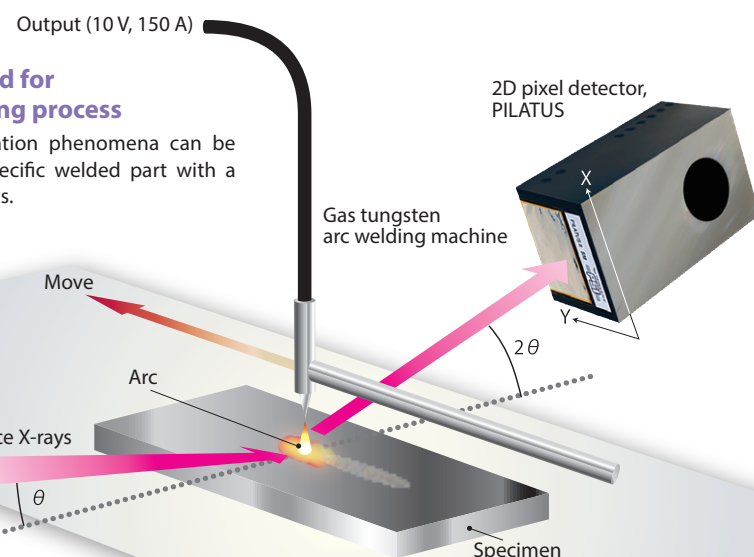
Niobium carbide (NbC) appears from a liquid phase after a few seconds of rapid cooling, and grows stably. As a result, its microstructure is stabilized and solidification crack is suppressed.

- (1) First, the metal melts and the temperature decreases. At the moment the metal starts to solidify, a δ phase first appears from a liquid phase (halo pattern).
- (2) A γ phase appears with further decreasing temperature.
- (3) When the temperature further decreases, NbC appears (is crystallized) and the liquid phase disappears. At this time, the γ -phase and NbC spots are aligned, indicating a structurally stable crystal orientation.
- (4) Finally, a γ + δ +NbC triple phase forms.

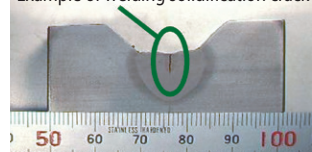


Equipment developed for observation of welding process

The melting and solidification phenomena can be observed in situ at the specific welded part with a high time resolution of 0.01 s.



Example of welding solidification crack



Control of Conditions of Finished Surface of Alloyed Hot-Dip Galvanized Steel Sheets

Elucidation of alloying reaction inside zinc coating

Achievements

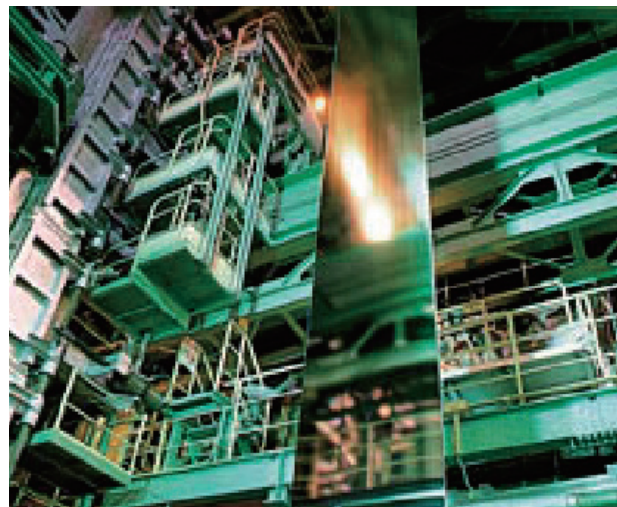
- Clarification of growth behavior of an iron-zinc (Fe-Zn) alloyed layer in an **alloyed hot-dip galvanized steel sheet*** by real-time in situ observation during the alloying process
- Establishment of guidelines for creating a smooth and durable coating surface

R&D facility: Sumitomo Metal Industries, Ltd.

***Alloyed hot-dip galvanized steel sheet:** Hot-dip galvanized steel sheets are obtained by coating zinc (Zn) over a steel sheet surface. These sheets have been used for many years because of their excellent corrosion resistance. However, small swellings are generated under the Zn coating after galvanization, causing the delamination of the coating and the deterioration of weldability. These problems can be solved by changing the Zn coating into an Fe-Zn alloy through heat treatment after hot-dip galvanization. The thus-obtained alloyed hot-dip galvanized steel sheet has been widely used in automobiles in recent years.

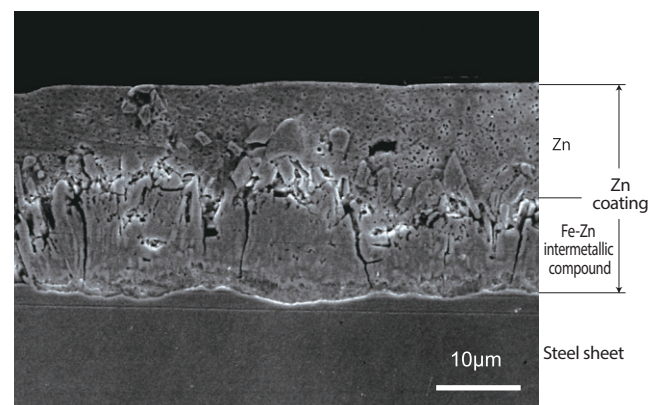
Hot-dip galvanizing line

Zn is attached to a continuously moving steel sheet.



Structure inside coating of alloyed hot-dip galvanized steel sheet (SEM image)

The figure below shows an SEM cross-sectional image of a Zn coating that was cooled in the middle of an alloying reaction. Fe-Zn intermetallic compounds are grown on the interface between the Zn coating and steel sheet.



Role of SPring-8

Background

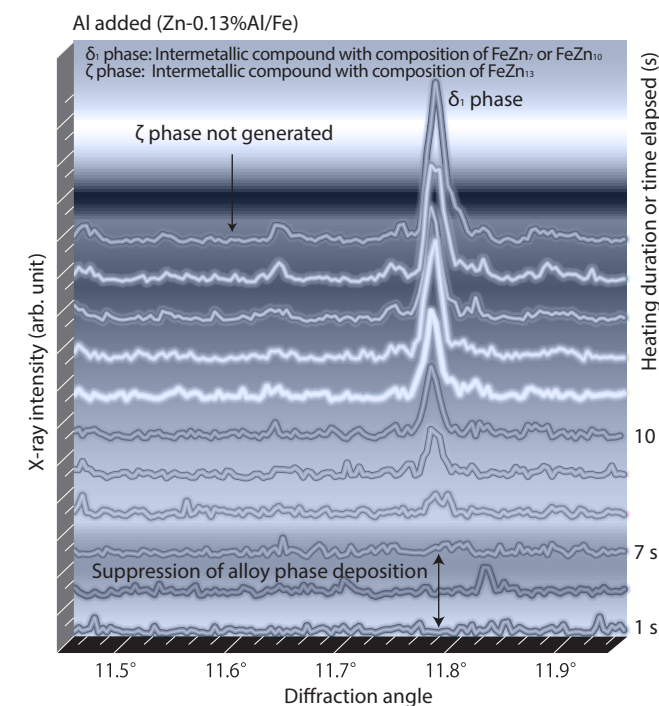
The condition of the finished surface of alloyed hot-dip galvanized steel sheets is considerably affected by the initial formation behavior of Fe-Zn intermetallic compounds in the Zn coating. Hence, it was necessary to understand the entire process of the formation of Fe-Zn intermetallic compounds including the initial formation.

Thus far, the observation and measurement had been carried out after temporarily cooling a heat-treated hot-dip galvanized steel sheet to stop the formation of intermetallic compounds in the Zn coating. Therefore, the initial formation behavior of intermetallic compounds had not been clarified.

Results

We succeeded in the real-time *in situ* observation of the process by which Fe-Zn intermetallic compounds are grown in the Zn coating of an alloyed hot-dip galvanized steel sheet from the initial stage using the high-brilliance X-ray at SPring-8.

The analysis result of **X-ray diffraction profiles** obtained in real time revealed that the growth rate of Fe-Zn intermetallic compounds depends on the diffusion velocity at which Fe atoms are mixed with Zn atoms, rather than the rate at which Fe atoms react with Zn atoms to form Fe-Zn intermetallic compounds, even at the initial stage of the growth. From this result, we established guidelines for technologies to control the initial stage of the formation of intermetallic compounds, which is important for creating smooth coating surfaces.

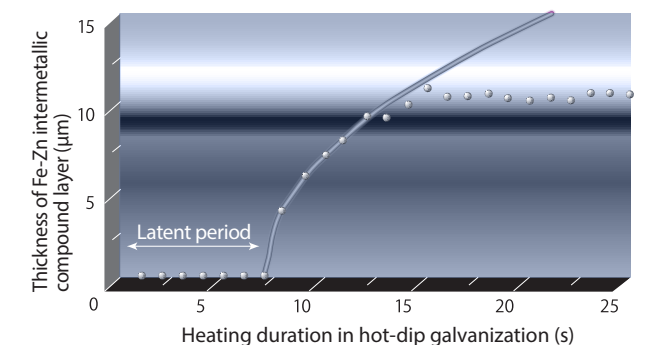


X-ray diffraction profile associated with heating of hot-dip Zn coating

Formation of the Fe-Zn intermetallic compounds is prevented for 7s after the Zn coating melts; then, Fe-Zn intermetallic compounds are formed. This indicates that a small amount of aluminum (Al) added to Zn forms an Fe-Al intermetallic compound layer on the interface between the Zn coating and steel sheet, preventing the reaction between the two; subsequently, Fe-Zn intermetallic compounds form after this Fe-Al intermetallic compound layer disappears.

Formation behavior of Fe-Zn intermetallic compound

The thickness of the Fe-Zn intermetallic compound layer increases in proportion to the square root of time after the melting of the Zn coating during the formation process. This indicates that the growth rate of the Fe-Zn intermetallic compounds is determined by the diffusion velocity of Fe atoms being mixed with Zn atoms.



SPring-8 contributes to the Development of Industries in addition to Academic Research.

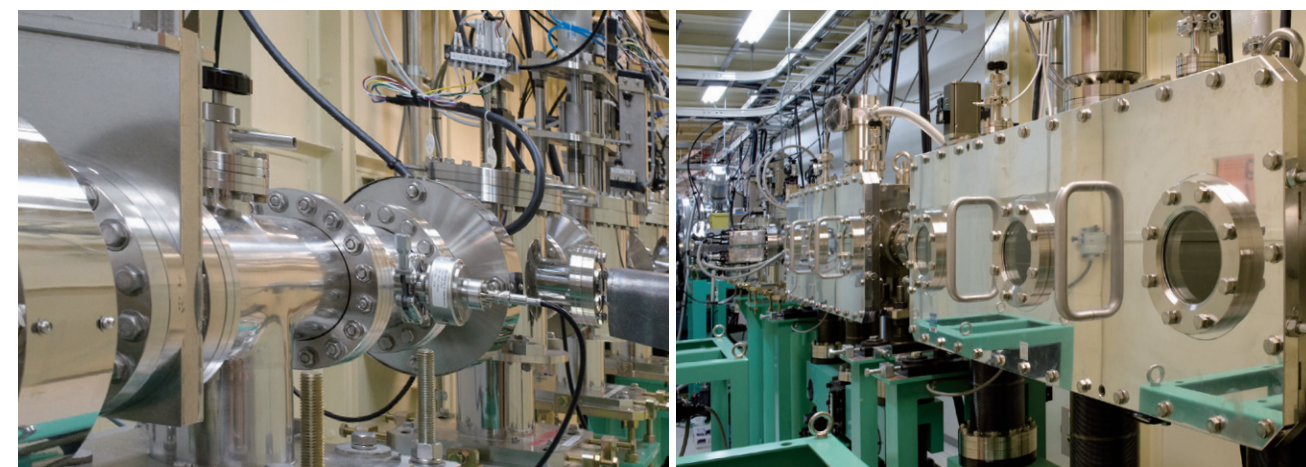
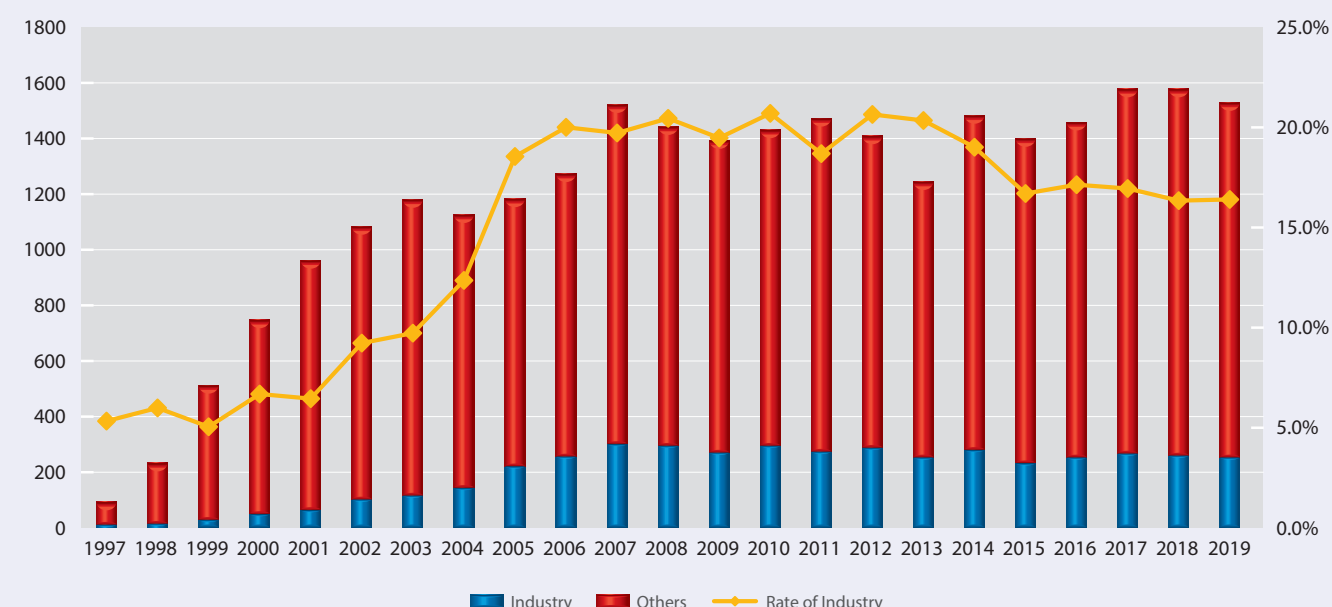
SPring-8 was constructed at a great cost of about 110 billion yen in 1997 and has an annual maintenance cost of about 8.5 billion yen. Large facilities such as this have a major responsibility to maximize the use of their technologies, not only at the frontier of scientific research, but also for industry.

To accelerate the industrial application of SPring-8, JASRI introduced a coordinator system in FY2000, started operating public beamlines (currently three beamlines) specialized for industrial application in FY2001, and established the Industrial Application Division in FY2005, thus continuing technological development with the convenience of users. Moreover, trial uses (trial,

FY2002; systemized in FY2003–2005) and the Program for Strategic Use of Advanced Large-scale Research Facilities (FY2005–2006) were implemented. In addition, Feasibility Study Proposals for Industrial Application, which provide potential users of SPring-8 with the all-year-round opportunity to use SPring-8 through a simple application process, have recently been established.

The industrial applications of SPring-8 have expanded yearly as shown in the figures owing to the improvement of the facility and its systems, and the implementation of programs. Not only has the number of users increased, but we have also seen users from new kinds of industry during this period.

Number of Conducted Proposals at Public BLs by Affiliation



SPring-8 Measurement Service provides measurements using SPring-8 performed by staff of the Industrial Application Division of JASRI instead of users. Users can send samples to SPring-8 as well as visit SPring-8 and observe measurements. The samples are measured and will be returned to the users in a month.

The Measurement Service aims to increase the convenience of SPring-8 for research institutions and companies that have difficulty in securing in-house technical staff and to solve urgent requirements. The Service is regarded as one of the Proprietary Time-Designated Proposals in terms of service cost. The cost to users is the sum of the beamtime fee (JPY 180,000 per 2 h), the fixed fee for consumable materials (JPY 2,680 per 2 h), and the variable fee for materials actually used during measurements.

If you are interested in or wish to know more about the industrial applications of SPring-8, please visit our website (<http://www.spring8.or.jp>), where you can find many examples of industrial applications. If you wish to use SPring-8 or find out whether the measurements you require are possible, please contact our coordinators in the Industrial Application Division (Phone: +81-(0)791-58-0924, E-mail: support@spring8.or.jp). They will help you use our facility if you are unfamiliar with the use of synchrotron radiation. We hope that you will make active use of our facilities.

We continue to promote industrial applications of SPring-8 capabilities, which would be available by implementing the top-notch measurement technologies.

Publication: Japan Synchrotron Radiation Research Institute (JASRI)

Photos and images provided by: Toyota Motor Corporation; Daihatsu Motor Co., Ltd.; Sumitomo Rubber Industries; Kracie Home Products, Ltd.; Ezaki Glico Co., Ltd.; Miyoshi Oil & Fat Co., Ltd.; Mitsubishi Electric Corporation; Sumitomo Bakelite Co., Ltd.; Ozeki Chemical Industry Co., Ltd.; Asahi Kasei Corporation; Asahi Kasei Construction Materials Corporation; Fujitsu Laboratories Limited; Sumitomo Electric Industries, Ltd.; GS Yuasa Corporation; Toshiba Corporation; Tokyo Chemical Industry Co., Ltd.; NIPPON STEEL Stainless Steel Corporation and Osaka Prefecture University; NIPPON STEEL CORPORATION

©All rights reserved. January, 2021