Successful Results of Industrial Applications at SPring-8
Industrial applications account for more than 20% of the total number of research proposals carried out at SPring-8. The world’s highest measurement and analysis technologies with high-performance synchrotron radiation have become essential for material evaluation for manufacturing in companies.

This booklet is a collection of research proposals with industrial applications conducted at SPring-8, the achievements of which are presented to be easily understood by people outside the field of expertise. This booklet was prepared for general readers to easily comprehend the contents when they see the title and the “achievements” in the blue box. Such clear and simple explanations have been strongly requested by the managers of companies using or considering the use of SPring-8 as well as by the politicians and policymakers who determine the social significance of SPring-8. I hope that this booklet will help such people and the general public to understand the contribution of SPring-8 to industry.

I sincerely appreciate the cooperation of the many parties involved, including those from companies involved in the preparation of this booklet.

Yoshiharu Doi, President
Japan Synchrotron Radiation Research Institute (JASRI)
Exhaust gas is purified through catalytic reactions when three-way catalysts are used.

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.

The components of exhaust gas from automobiles are oxidized or reduced by the action of catalysts and thus the exhaust gas is purified. Three-way catalysts promote the simultaneous detoxification of these 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.


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 these 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.

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.

Role of SPring-8


Research method

- X-ray absorption fine structure (XAFS)

Background

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Realization of Intelligent Catalyst for Automotive-Emissions Control

Clarification of self-regenerating mechanism to maintain catalytic activity

Achievements

- Atomic-level clarification of the mechanism of “intelligent catalysts” - a catalytic precious metal renews itself using special ceramic materials
- Substantial reduction of precious metal usage by intelligent catalysts using precious metals, such as palladium, platinum, and rhodium
- Contribution to environmental purification and resource saving from the installation of intelligent catalysts on more than 4 million automobiles as of July 2008

R&D Facility: Daihatsu Motor Co., Ltd., and Japan Atomic Energy Agency

*Intelligent catalyst: Automotive catalysts deteriorate as a result of a decrease in the active surface area of the precious metals, and this is caused by the growth of metal grains under the inherent redox environment of exhaust gases at high temperatures. We developed self-regenerating catalysts in which precious metals were coordinated as ions into special ceramic crystals (a perovskite oxide). The self-regenerating catalyst, which suppresses the grain growth of precious metals, are based on the repeated movement of the precious metals in and out of perovskite crystal between a solid solution and metallic nanoparticles during the natural changes in the redox conditions. That is, the newly developed catalysts have a self-regenerating function to change their structure in accordance with the environment. Intelligent catalysts were thus named to reflect this function.

Background

The performance of automobile catalysts deteriorates with increasing mileage. Therefore, an excess amount of precious metals is required to maintain the catalytic performance throughout the life of an automobile; but from the viewpoint of over-consumption and supply problems of precious metals, it is necessary to suppress the deterioration of automobile catalysts.

We developed intelligent catalysts with a self-regenerating function using a new concept. However, conventional methods were insufficient to clarify the mechanism at an atomic level.

Role of SPring-8

The crystalline structure of the perovskite oxide was examined in detail using the high-brilliance X-ray at SPring-8, which is suitable for measuring the properties of precious metals. As a result, it was clarified that precious metal ions repeatedly move in and out of the crystals depending on the state of the exhaust gases, thereby maintaining sufficient catalytic performance.

We developed a number of self-regenerating ceramic materials by applying this technology, and succeeded in substantially reducing the use of precious metals. This technology is attracting attention worldwide as a new means of solving environmental and resource-related problems at the same time.

Mechanism of self-regeneration of intelligent catalyst

Precious metal ions are coordinated in the form of a perovskite oxide precipitate from the crystals and form nanosized precious metal particles under an oxygen-deficient condition. The ions diffuse into the crystals under an excess-oxygen condition, and the particles return to an atomic size. Intelligent catalysts maintain their high catalytic activity by restoring the size of particles through this mechanism.

Change of precious metal catalyst in exhaust gases

The gases exhausted from automobiles repeatedly change its state between oxidizing and reducing states several times per second. Catalysts are exposed to temperatures as high as 1000°C under such an atmosphere. Precious metal particles are gradually enlarged in the presence of conventional catalysts. In contrast, precious metal particles can maintain their highly active fine size in the presence of intelligent catalysts.

Results

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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.

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.

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.

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.

Role of SPring-8

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 polymers and to increase the dispersibility of the silica.
Development of Hair-Care Products That Make Hair Shiny

Quantification of hair shine at the cellular level

Achievements

- Cellular-level quantitative evaluation of hair curliness related to the shine of hair
- Commercialization of hair shampoos, conditioners, and treatments containing an organic acid that can suppress hair curliness and restore shine to hair.

R&D facility: Kao Corporation

Background

Many women worry about losing the shine of their hair with aging, but the causes behind this loss have remained unclear. First, the degree of hair shine was evaluated quantitatively, and it was clarified that hair shine decreases with aging. It was found that the decrease in the degree of shine is related to the increase in the curliness of hair. Furthermore, the observation of the cortex cells* inside hair by dyeing revealed that the two types of cell in a curly hair were unevenly distributed in the hair.

Results

It is necessary to examine how the cells with twisted internal fibers are arranged in order to clarify the relationship between the uneven distribution of cortex cells and the curliness of hair. Unfortunately, a hair is 100 μm in diameter (1 μm is one-thousandth of 1 mm). Only the high-performance X-ray at SPring-8, with a high-accuracy analysis capability at a resolution of 5 μm, offers a sufficiently high resolution to observe and analyze the structure of fine regions in a hair. From the analysis of the images obtained by the small-angle X-ray scattering technique**, it was quantitatively clarified that the curliness of a hair is related to the degree of distributional inhomogeneity of the two types of cortex cells.

Changes in hair with aging

Human hair becomes curlier with aging and also loses its shine. The cross-sectional images of dyed hair revealed that the two types of internal cells (red and green) are each distributed on one side of a curly hair.

Distribution of cells inside curly hair

The cells with parallel internal fibers (green part) and those with twisted internal fibers (red part) are each distributed on one side of the hair.

Images obtained by small-angle X-ray scattering technique

The circle at each center shows the shadow of the beam stop. Black parts left and right of the circle show the scattering pattern that indicates the arrangement of internal fibers in the hair. The pattern for a straight hair has only minor differences between the inner and outer sides, whereas a curly hair has a different pattern on each side.
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.

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

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

Hair-protective and -beautifying effects of inositol

Permeability of inositol into the hair

Numbers in the legend of the figures below represent the concentration of inositol in the hair. 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 highest 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.

Un treated

Inositol treated

Inositol stays inside the hair even after rinsing, resulting in continuous 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.

*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.

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

**Background**

When early-stage caries advances, the tooth surface is eroded and tooth cavities (carious 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.

**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.

**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**

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

**Changes in mineral content**

Measured using conventional transverse microradiography

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

**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.


**Role of SPring-8**

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 showed 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.
Development of Long-Lasting Artificial Joints
A new direction in designing materials to prevent oxidation and degradation of artificial joints

**Achievements**

- Development of the first artificial joint consisting of **ultra-high molecular weight polyethylene** containing vitamin E to prevent oxidation and degradation.
- Contribution to product management and future materials design through confirmation of antioxidant capability of vitamin E by precisely analyzing trace amounts of vitamin E.
- First observation of the age-related deterioration of artificial joints at the crystallographic level.

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**Background**

The frequency of joint replacement procedures has been rising in recent years. However, patients with osteoarthritis who received joint replacements in their 60s need to have another replacement surgery in their 80s because existing artificial joints last only 10–20 years. Therefore, development of long-lasting artificial joints has been a major priority.

Polyethylene, which has been commonly used in artificial joints, is degraded through oxidation. To overcome this issue, research on antioxidants has been conducted, resulting in the development of UHMWPE containing vitamin E, which has fewer side effects in the human body. UHMWPE containing vitamin E is resistant to oxidation, and has improved lubrication relative to traditional polyethylene. A clinical study of UHMWPE, involving 65 patients, was conducted in 2004.

**Results**

It will take another 5–10 years to demonstrate that polyethylene containing vitamin E is actually resistant to oxidation. However, before UHMWPE can be commercialized, the antioxidant capability must be confirmed. To this end, a trace amount of vitamin E contained in artificial joints was precisely examined using SPring-8’s highly brilliant infrared synchrotron radiation. This examination elucidated the relationship between the additive amount of vitamin E and antioxidant capability, leading to the commercialization of the artificial joints as early as 2010.

Moreover, a small-angle X-ray scattering (SAXS) technique at SPring-8 revealed that age-related degradation of polyethylene can be analyzed by studying changes in the material’s crystal structure. This technique could also be applied to other products containing vitamin E, allowing an understanding of their age-related degradation and a demonstration of their long-term usefulness.

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**Research method**

- X-ray scattering pattern of polyethylene used as an artificial knee joint.
- Small-angle X-ray scattering (SAXS) technique at SPring-8.
- Measured SAXS data from an artificial joint used in the human body for 14 years. The scattering pattern can provide information about the crystal structure.
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.

Achievements

- 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.

Formation of polymer-modified cement waterproofing coating

1. Combine inorganic ceramic containing alumina and polymer emulsion.
2. EVA resins, the alumina ceramics, and the aggregate are uniformly dispersed in the water in the emulsion by kneading.
3. The cement components are separated from the alumina ceramics in the water in the emulsion.
4. The separated cement components hydrate using the water in the emulsion, and the water is consumed. Simultaneously, the EVA resins start fusing.
5. Moisture divergence and fusion of the EVA resins are promoted by further hydration, and a coupled waterproofing coating is formed.

Hydration processes at room temperature and 35°C

Hydrates are produced faster at 35°C than at room temperature. This result revealed that hydration is promoted with increasing temperature.

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

CA, C3AH6, C2AH8, Temperature of sample

Hydrates are produced faster at 35°C than at room temperature. This result revealed that hydration is promoted with increasing 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.

Role of SPring-8

Research method

X-ray diffraction/scattering

Beamline used at SPring-8: Engineering Science Research I (BL19B2)

Achievements

- X-ray diffraction experiment at SPring-8: Two-dimensional pixel detector, PILATUS
- High-intensity X-ray at SPring-8: Tobermorite crystal

Results

- Analysis of formation mechanism of crystalline component tobermorite
- Clarification of formation mechanism of tobermorite

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

X-ray diffraction pattern observed 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 clarified.


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.

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**Background**

Measures to abolish the use of Cr⁶⁺ are being increasingly carried out because of the damage to human bodies caused by Cr⁶⁺ 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 Cr⁶⁺ through chemical treatment. What we need is a nondestructive analytical method of detecting Cr⁶⁺.

In the method of analyzing Cr⁶⁺ through chemical treatment, Cr⁶⁺ is extracted by dissolving a chromate coating in unheated or hot water. In line with this, the following problems occur. The valency of Cr⁶⁺ changes during extraction, Cr⁶⁺ 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, Cr⁰ and Cr³⁺ were observed to be clearly separated in the absorption spectra. We measured and clarified the absolute amount of Cr⁶⁺ (content rate) for various chromate coatings by the XAFS method. Moreover, it has become possible to obtain the depth distribution of Cr⁶⁺ in chromate coatings from the dependence of X-ray injection angle in the XAFS result. Thus, the technology for directly analyzing Cr⁶⁺ in chromate coatings without chemical treatment was improved.

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

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*Chromate coatings are used for protecting iron and aluminum from corrosion. Some contain hexavalent chromium (Cr⁶⁺) and others contain trivalent chromium (Cr³⁺). Chromate coatings containing Cr⁶⁺ include yellow and black chromates and iridite. Cr⁶⁺ is a hazardous substance and causes diseases such as skin ulcers, nasal septum perforation, and lung cancer, and hence, the use of Cr⁶⁺ has started to be regulated. Cr³⁺, less hazardous to human bodies than Cr⁶⁺, has been studied for use in chromate coatings instead of Cr⁶⁺.

**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. Cr⁶⁺ is included in the list of regulated substances.
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%

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

R&D facility: Sumitomo Electric Industries, Ltd.

**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.

Recycling process of tungsten

Used carbide tools are dissolved in molten salt to obtain a Na2WO4 solution. The solution is introduced into an ion exchange resin to collect tungsten ions in the (NH4)2WO4 solution, which is then heated and condensed so that it crystallizes as ammonium paratungstate (APT). APT is oxidized by roasting to obtain WO3, which is then reduced to tungsten. The obtained tungsten is reacted with carbon to form the reusable tungsten carbide (WC).

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.

Role of SPring-8

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, WO42-, HW6O215-, and H2W12O406-, 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 H2W12O406- ions, which contain the most tungsten atoms of the three species, still remained in the resin.

XAFS measurement results for adsorbed ions remaining in resin during ion exchange of H2W12O406-

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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.

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**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.

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**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 Ni²⁺ that replace some of the Li⁺ upon repeated charging and discharging.

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**Publication**


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**Role of SPring-8**

**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 Ni²⁺ 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.

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*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.
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

**Research method**

- X-ray diffraction/scattering

**Clarification of the relationship between the crystal structure of electrode materials used in nickel-metal hydride batteries**

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 (AB-type alloy) as the anode material is at least 85% of the theoretical value; therefore, the further improvement of the capacity is difficult.

**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.

**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.

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*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.

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**Beamline used at SPring-8:** Engineering Science Research I (BL19B2)

**Award for this research:** The 7th Hyogo SPring-8 Award (2009)
Contribution to Development of Next-Generation CMOS Products
Development of technology for evaluating ultrathin-film laminated structures

Achievements

- Realization of high-precision evaluation of film thickness, flatness, and density distribution by developing a technology for measuring characteristics such as the thickness of ultrathin films with a sensitivity 5 orders higher than that of conventional technologies
- Establishment of process conditions for manufacturing next-generation CMOS* products with high reliability
- Tremendous contribution of this evaluation method to the development of CMOS products produced on an approximately 2 trillion yen scale in Japan.

R&D facility: Fujitsu Laboratories, Ltd.

*CMOS stands for complementary metal oxide semiconductor, a type of semiconductor structure; the abbreviation CMOS is commonly used. Both p- and n-type transistors are used in CMOSs. Most semiconductors currently used, such as those in the CPU of PCs, have a CMOS structure.

Research method

- X-ray diffraction/scattering

Achievements

- Role of SPring-8

Evaluation of gate insulating film structure

The measurable intensity of an X-ray reflected from a thin film, which conventionally has a range of up to 7 orders, was measured over a range of 12 orders by applying the high-brilliance SPring-8 X-ray. The detectable angular range (2θ) of the reflected X-ray was widened from 7° to 40°. As a result, the evaluation of the properties of ultrathin films as thin as 1 nm became possible.

Interference pattern due to difference in film density (triple-layer model)

Results

When SPring-8 high-brilliance X-rays are irradiated onto an ultrathin film, an X-ray reflected from the film surface interferes with an X-ray that has passed through the film and has been reflected from its bottom surface, i.e., the border with the substrate. This interference pattern is used to obtain the refractive index of the film, from which the film density is calculated. In addition, the roughness of the film surface can be measured because the attenuation of the reflectance of X-rays depends on the incident angle.

We elucidated, by quantitative analysis, that the leakage current increases owing to the nonuniformity in the thickness of the SiO$_2$ film, which serves as the gate insulating film, and in the distribution of the added nitrogen. Thus, the optimal conditions for fabricating uniform insulating films were successfully established.
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

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.

Measurement of photoelectron spectra under voltage application

With 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.

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

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*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-Kα (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.
Development of Photonic Integrated Devices with High Luminescent Efficiency

Clarification of factors improving luminescent characteristics

Measurements of the composition of the laser active layer in photonic integrated devices* at high accuracy

Contribution to the improvement of the luminescent efficiency of photonic devices by approximately 40% through optimization of the composition and the commercialization of high-performance photonic integrated devices

R&D facility: NEC Corporation and Himeji Institute of Technology (now University of Hyogo)

*Photonic integrated device: A device comprising various optical elements, such as semiconductor lasers, optical waveguides, optical switches, optical modulators, and optical detectors. The photonic integrated element introduced here incorporates a modulator and a semiconductor laser on a single semiconductor substrate. This is a key device for optical communication systems to realize higher capacity optical communications because multiple signals with different wavelengths can be superimposed on a fiber.

**Lattice constant:** Six constants that represent the lengths and angles between crystal axes.

Background

The luminescent characteristics of photonic integrated elements (luminescence intensity for each wavelength) depend on the quality of the laser structure. A selective-area growth method, in which the crystals of the laser active layer (InGaAsP layer) are grown between SiO₂ masks, has been developed as a method of fabricating laser structures. This method enables us to short en the fabrication process compared with conventional methods, resulting in a low production price.

However, it was impossible to accurately control the quality of crystals of InGaAsP layers, because the layer width is as narrow as 1.5 μm and thus there was no method of measuring the composition of the layers with high accuracy.

Results

It is necessary to measure the lattice constants** to determine the composition of InGaAsP layers. For this, an X-ray diffraction measurement method was spatial resolution of a few μm or higher is required. This measurement was realized using the synchrotron radiation of SPring-8. As a result, the composition of InGaAsP layers, which depends on the mask width, was analyzed with an accuracy at least one order higher than before. In addition, we unveiled an unconventional result that the composition ratio of group V elements (As and P) in InGaAsP layers changes depending on the mask width. Using the above results, it became possible to control the composition and lattice constants of crystals selectively grown in devices as designed.

Structure of photonic integrated device with modulator and laser

It is necessary to fabricate elements such that the pitch of diffraction lattices, the short absorption wavelength of a modulator, and the wavelength of peak gain in a laser region are synchronized.

Selective-area growth of laser activation layer

When the compounds of source gases are diffused onto the surface of an InP substrate partially masked with SiO₂ or other films, crystals grow on the surface via a thermal decomposition reaction. This is a selective-area growth method that enables the selective-area growth of the crystals in InGaAsP layers in regions other than the masks. The method can also be used to realize waveguides (Eg1 and Eg2) with different compositions.

Change in SiO₂ mask width and composition ratio of group V elements (As and P) in InGaAsP layer

The lattice constants of an InGaAsP layer (0.1-0.2 μm thick, 2-30 μm wide) that acts as a laser activation layer were measured using an X-ray microbeam generated from high-brilliance synchrotron radiation. The results revealed that the composition ratios of not only group III elements (Ga and In) but also group V elements (As and P) in the InGaAsP layers change depending on the SiO₂ mask width (Wm).

Achievements

- Measurements of the composition of the laser active layer in photonic integrated devices* at high accuracy
- Contribution to the improvement of the luminescent efficiency of photonic devices by approximately 40% through optimization of the composition and the commercialization of high-performance photonic integrated devices

Role of SPring-8

Beamline used at SPring-8: Hyogo ID (BL24XU)

Establishment of Design Guidelines for Oriented Film Materials Used for Liquid Crystal Displays

Elucidation of factors determining the orienting power for liquid crystals

Research method

X-ray diffraction/scattering

Achievements

1. Finding that the orienting power of oriented films* determining the quality of liquid crystal displays is closely related to the degree of crystallization** of the oriented film surface
2. Establishment of guidelines for designing materials used in oriented films with high orienting power for liquid crystals


*Liquid crystal oriented film: Liquid crystal displays can reproduce images by varying the alignment of liquid crystal molecules so that light is transmitted or blocked. An oriented film, a necessary component for aligning liquid crystal molecules unidirectionally, comprises a substrate coated with a grooved polymer film. Liquid crystal molecules are aligned in the groove direction when they come into contact with the oriented film. The quality of displays depends on the state of this alignment.

**Degree of crystallization: Percentage of a crystalline substance consisting of both crystalline and amorphous phases.

Principle of liquid crystal display

Two oriented films sandwich liquid crystal molecules and are placed so that the directions of their grooves are 90° different from each other. Accordingly, the lines of liquid crystal molecules are twisted by 90°, thus traveling light is twisted through them. The light is guided to one of the polarizing plates (which transmit light in only one direction) that are placed outside the oriented film. When a voltage is applied between the two oriented films, each liquid crystal molecule becomes perpendicular to the films, hence, the light travels straight and cannot pass through the second polarizing plate, the polarizing direction of which is at an angle of 90° to that of the first polarizing plate. The light is thus controlled by turning the voltage on or off.

Quality of display

Liquid crystal molecules are orderly aligned with higher orientation.

The display can show clear images.

Liquid crystal molecules are disorderly aligned with low orientation.

The display has a low performance.

Measurement results for liquid crystal oriented film (surface)

The peak of scattering intensity becomes high with a higher degree of crystallization (higher orienting power) at the oriented film surface.

Results

First, the degree of crystallization of liquid crystal oriented films was measured using the high-brilliance X-ray of SPring-8 and its high-precision measurement system. The result indicated that the degree of crystallization was different between the oriented film surface in contact with liquid crystal molecules and deep in the film. In addition, oriented films with different orienting powers were examined by grazing incidence X-ray diffraction. We clarified that the higher the degree of crystallization at the oriented film surface in contact with liquid crystal molecules, the better the orienting power. The orienting power was not affected by the degree of crystallization deep in the film.

We can now design the materials for oriented films using the above results as guidelines.


Beamline used at SPring-8: Engineering Science Research I (BL19B2)
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

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.

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

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.

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.

Results

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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

Research method

- X-ray diffraction/scattering

Award for this research:
- The Japan Institute of Metals Best Paper Award for Materials Processing (2007)
- The Japan Welding Society Paper Award (2007)
- The Iron and Steel Institute of Japan Paper Award (2008)

Beamline used at SPring-8: Engineering Science Research III (BL46XU)

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 sec.

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 y-phase and NbC spots are aligned, indicating a structurally stable crystal orientation.
4. Finally, a γ+δ+NbC triple phase forms.

Halo pattern: Ring-shaped wide pattern observed in the presence of a liquid phase

Nbc: Niobium carbide
δ phase: Primary phase of Fe-Ni-Cr alloy
γ phase: Secondary phase of Fe-Ni-Cr alloy

Halo pattern image


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.

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.

Role of SPring-8

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 week 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.

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*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.

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

Elucidation of alloying reaction inside zinc coating

**Research method**

- X-ray diffraction/scattering

**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

**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.

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.

**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.

**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.

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

The figure 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.

**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.

**Formation of the Fe-Zn intermetallic compounds**

Formation of the Fe-Zn intermetallic compounds is prevented for 7 s 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 the Fe-Al intermetallic compound layer disappears.

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

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In-Vacuum Undulator Developed in Japan
Highly efficient production of the world’s greatest synchrotron radiation

**Achievements**

- Realization of the world’s first **in-vacuum undulator** to produce high-brilliance synchrotron radiation at SPring-8
- Production and export of in-vacuum undulators to countries including the United States, Australia, Switzerland, and Korea
- Application of in-vacuum undulators to the **X-ray free electron laser (XFEL)**, an extremely intense new light, and successful oscillation of an X-ray laser at SACLA

**R&D facility: RIKEN and others**

*In-vacuum undulator*: Synchrotron radiation is generated when an electron beam traveling nearly at the speed of light is bent using a magnet. This is achieved using an undulator. Magnets are placed outside the vacuum tank in conventional undulators. In contrast, magnets are placed inside the vacuum tank in in-vacuum undulators, enabling us to place the magnets closer to the electron beam to apply high-intensity magnetic fields. It is thus possible to generate high-brilliance X-rays in a highly efficient way.

**X-ray free electron laser (XFEL)**: A new laser in the X-ray region produced artificially. An accelerated high-quality electron beam injected into an in-vacuum undulator generates X-rays, and the interaction between the X-rays and the electrons in the in-vacuum undulator produces the XFEL. The XFEL is a billion times brighter than the X-rays of SPring-8 in specific ranges of wavelength. More detailed structures of materials, for example, the structures of proteins will hopefully be observed.

Mechanism of in-vacuum undulator

An electron beam is introduced between two rows of magnets, with the appearance of a harmonica, whose N and S poles are alternately aligned. The electron beam traveling in the magnetic fields periodically meanders, and synchrotron radiation is generated each time the beam direction changes. A high-brilliance light with a specific wavelength is produced by making the synchrotron radiations thus generated interfere with themselves.

Undulator for XFEL (Vacuum tank removed)

Conventional undulator

- Magnets
- Vacuum tank
- Electron beam

In-vacuum undulator

- Magnets
- Electron beam
- Synchrotron radiation

In-vacuum undulators manufactured in Japan have been exported since around 2000. Some undulators around the world have also been developed whose designs were based on these Japanese models.

**Background**

Undulators must be designed to have a short period length of a series of magnets to obtain short-wavelength high-brilliance X-rays. It is also necessary to narrow the vertical gap between magnets to achieve the magnetic field required. However, narrowing the vertical gap in conventional undulators is difficult because the vacuum tank is placed between magnets. In-vacuum undulators were developed to solve this problem. It is possible to narrow the vertical gap to as short as possible unless the electron beam is blocked, because a line of magnets is placed inside the vacuum tank in in-vacuum undulators.

**Results**

However, we had to wait for cutting-edge technology to be developed, such as the realization of a high degree of vacuum and a means of preventing the dissipation of magnetic forces, to put in-vacuum undulators into practice. A pilot in-vacuum undulator was developed at the High Energy Physics Laboratory (currently, High Energy Accelerator Research Organization) in Tsukuba, Ibaraki, in 1990. A full-scale in-vacuum modulator was also introduced at SPring-8, which has equipment for generating the world’s highest-level X-rays with short wavelengths and high brilliance. Currently, 27 undulators are running at SPring-8. One of these undulators is 25 m long, making it the world’s largest undulator, although most of them are 4.5 m long.

In-vacuum undulators have also started to be used in medium-sized synchrotron radiation facilities because of their capability to generate X-rays even at low electron energy.

Japanese in-vacuum undulators playing active roles around the world

In-vacuum undulators manufactured in Japan have been exported since around 2000. Some undulators around the world have also been developed whose designs were based on these Japanese models.
Future Expansion of Industrial Applications of SPring-8 and Improvement of Its Effects

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. A coordinating system was introduced in FY 2000 to promote the use of SPring-8 for industrial applications. Then, a public beamline specialized for industrial applications became operational in FY 2001 (3 beamlines are operational at present), and the Industrial Application Division was established in FY 2005. In addition, SPring-8 offered a program for trial users (attempted in FY 2002, systemized in FY 2003-2005) as well as a program for the strategic use of the large cutting-edge research facilities (FY 2005-2006).

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. There is still, we believe, room to explore new profitable uses of SPring-8. In addition, we are not only promoting the use of our established measurement technology for industry, but are also actively promoting the development of essential new measurement technology and attempting to breach the frontiers of current industrial technologies through collaboration with top academic institutions.

If you are interested in or wish to know more about the industrial applications of SPring-8, please visit our website (http://www.sprng8.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@sprng8.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.