NATIONAL INSTITUTE FOR MATERIALS SCIENCE

# NIMS NOW International

No. 1
2013 January-February

# Nothing is Unbreakable

## Reliability Assessment of Structural Materials Project

# *New Year's Greetings*

As we begin the year 2013, I would like to wish you all a wonderful new year.
It has now been 12 years since NIMS was established, and we are in the third year of the Third Five-year Plan Period. Today we have many signs that indicate NIMS has become a true Center of Excellence in materials science.

First of all NIMS has earned a high reputation at the world level, and many countries have approached us with requests for research collaboration. In 2012 alone we concluded 15 agreements for international scientific collaboration, as well as comprehensive collaborative agreements with 6 institutions. We also strengthened our collaboration with universities and research institutions in a number of countries, including France, Switzerland, Taiwan, and the United Kingdom, among others. NIMS also launched a new joint research center with Northwestern University (NU) in the United States, which is called NU-NIMS Center for Material Innovation. This center is the second joint international center for NIMS, following the establishment of TU-NIMS Joint Research Center with Tianjin University (TU) in China in 2011.

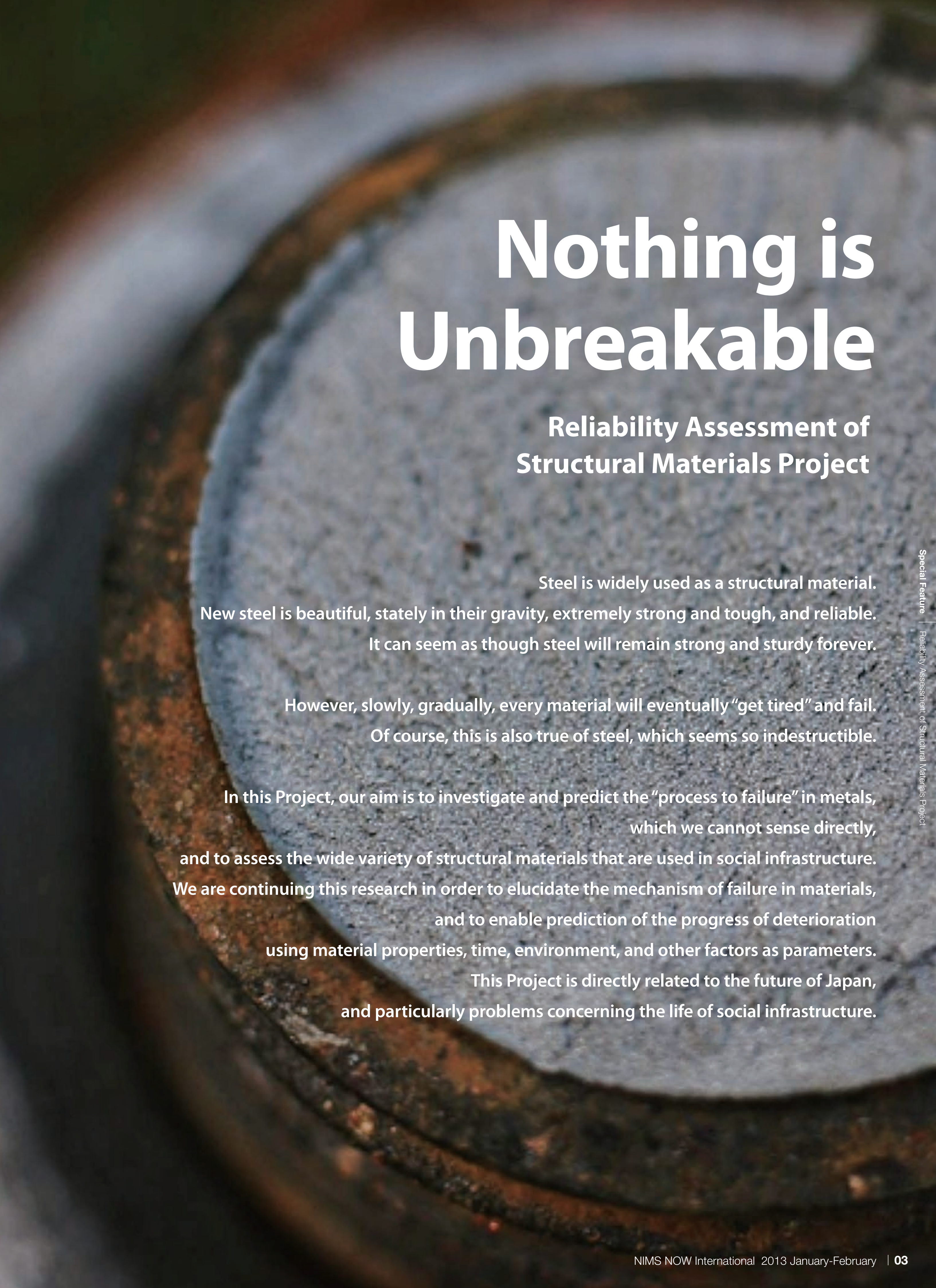
Increased collaboration with industry should also be mentioned. While this includes many international collaborative efforts, now NIMS is conducting a large number of joint research projects with Japanese companies through bilateral contract research and the new TIA Nano-Green Open Innovation Platform.

During 2012 NIMS also substantially expanded its services to Japanese research community through a series of new initiatives, which include Nanotechnology Platform, Center for Materials Research for Low Carbon Emission (CMRLC), Element Strategy Initiative Center for Magnetic Materials (ESICMM), Global Research Center for Environment and Energy based on Nanomaterials Science (GREEN), and TIA Nano-Green Open Innovation Platform. The NIMS Materials Database MatNavi was honored with the Commendation for Science and Technology by Japan's Minister of Education, Culture, Sports, Science and Technology (MEXT).

The international society is changing very rapidly, not only in the economic aspect, but also in terms of social systems. New nations are emerging as important players in manufacturing industries and other fields. On the other hand, as seen in recent years, the condition of the global economy remains difficult. In Japan we are searching for a new form of society. Precisely in times like these, creativity is vitally important. The development of human resources and their effective organization are essential for a prosperous society. Indeed it is the individual researchers who make new discoveries and innovations. From this viewpoint, we are devoting a great effort in nurturing its young researchers and also actively hiring and promoting women.

Often new ideas and innovations are generated through processes of interaction and discussion. To encourage interaction and discussion among our staff, we placed high priority in designing our new MANA/GREEN building to creating an environment where people can meet and actually see each other's faces for close interaction. I believe that the creativity nurtured in such an environment will produce a new era for Japan and for the world.

Prof. Sukekatsu Ushioda
President, National Institute for Materials Science



# Nothing is Unbreakable

## Reliability Assessment of Structural Materials Project

Steel is widely used as a structural material.
New steel is beautiful, stately in their gravity, extremely strong and tough, and reliable.
It can seem as though steel will remain strong and sturdy forever.

However, slowly, gradually, every material will eventually "get tired" and fail.
Of course, this is also true of steel, which seems so indestructible.

In this Project, our aim is to investigate and predict the "process to failure" in metals, which we cannot sense directly,
and to assess the wide variety of structural materials that are used in social infrastructure.
We are continuing this research in order to elucidate the mechanism of failure in materials,
and to enable prediction of the progress of deterioration
using material properties, time, environment, and other factors as parameters.
This Project is directly related to the future of Japan,
and particularly problems concerning the life of social infrastructure.

# Creep Strength Evaluation – Life Assessment of Thermal Power Plants

Creep Resistant Materials Group,
Materials Reliability Unit,
Environment and Energy Materials Division
**Kota Sawada**

## A new focus on thermal power

Today, thermal power generation technology is a focus of attention from two viewpoints. Firstly, since the nuclear power plant accident following the Great East Japan Earthquake of March 2011, thermal power has been a lifeline providing a stable supply of electric power for Japan. Secondly, because Japan's thermal power plants lead the world in generating efficiency, exports of this technology to countries around the world are expected to help revitalize the Japanese economy, while also realizing a substantial reduction in global $CO_2$ emissions.

Among thermal power plants, the generating efficiency of Japan's coal-fired thermal power plants ranks No. 1 in the world. The "ultra-super critical (USC) coal-fired thermal power plant," which is a state-of-the-art coal-fired thermal power technology, was realized by developing a high strength heat resistant steel called "high chromium steel," and 22 of these plants are now in operation in Japan.

## Creep strength and reliability of components of thermal power plants

In order to design the thickness of piping and other parts used in thermal power plants, the allowable stress of the materials used in those parts is necessary. Allowable stress is specified based on 100,000 hour creep rupture strength (100,000 hours = approx. 11.4 years) and other properties of the material. Accordingly, determining allowable stress with high accuracy results in improved material reliability.

Because it is particularly important to evaluate "100,000 hour creep rupture strength" with high accuracy, NIMS proposed a "region splitting analysis method" (Fig. 1), which is capable of evaluating the creep rupture strength of high chromium steel with high accuracy. This method is now gaining widespread acceptance.

Although allowable stress is determined by 100,000 hour creep rupture strength and other properties, many of the coal-fired thermal power plants that are actually in operation in Japan have already been in service for more than 100,000 hours. In order to maintain safe, long-term operation of these plants, it is necessary to know the "ultra-long term creep rupture strength" for operating periods exceeding 100,000 hours.

Figure 2 is a schematic diagram of the "stress – time-to-rupture curve" of high chromium steel. The solid line in the figure is an example of an evaluation line obtained by the above-mentioned "region splitting analysis method." Because very few experimental data are available for the time domain exceeding 100,000 hours, extrapolation is necessary, as shown by the dotted lines. However, in addition to the martensitic phase, the microstructure of high chromium steel contains a number of kinds of dispersed precipitates, and atomic diffusion causes microstructural changes under high temperature and long term conditions. Since the microstructural changes associated with this diffusion are assumed to become remarkable in the time domain exceeding 100,000 hours, prudent study of the appropriateness of the extrapolations shown in Fig. 2 is necessary.

Figure 3 shows the relationship between the precipitation temperature and precipitation time of the composite nitrides called the "Z phase" that precipitates in ASME Gr.91 steel. At the actual service temperature of 600°C, the Z phase can be observed for the first time when operating time exceeds 10,000 hours. Thus, it is important to predict "ultra-long term creep rupture strength" by first grasping the microstructural changes that occur in this long time domain, and then predict the microstructural changes in the long time domain exceeding 100,000 hours using a combination of experimental research and computational science.

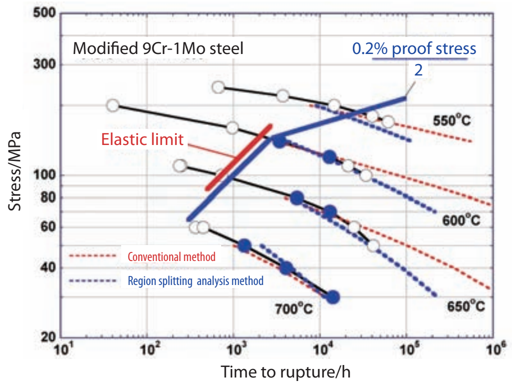



**Fig. 1** Creep strength of high chromium steel.

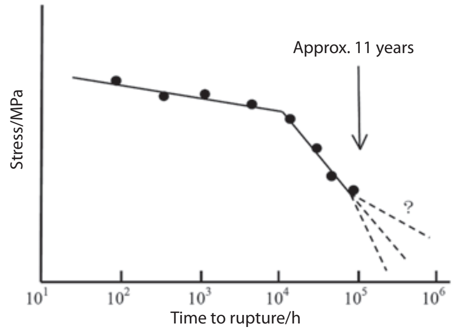



**Fig. 2** Prediction of ultra-long time creep strength (schematic diagram).

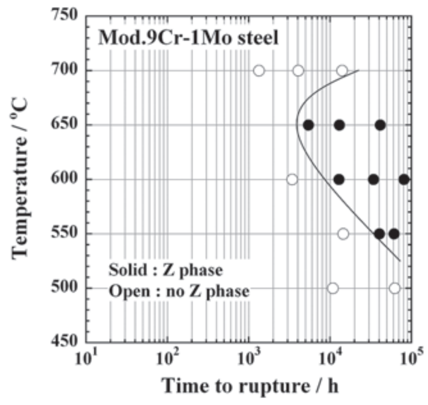



**Fig. 3** TTP diagram of Z phase.

**Kota Sawada** Ph.D.(Engineering) Completed the doctoral course at the Tohoku University School of Engineering in 1999 and joined the National Research Institute for Metals (NRIM; a predecessor of NIMS) as a Researcher in the same year. He was appointed NIMS Principal Researcher in 2012. His specialty is the science of high temperature strength.

# Evaluation of Gigacycle Fatigue Characteristics by Ultrasonic Fatigue Testing

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## Research on fatigue has a history of more than 100 years

Even though research on fatigue has a history of more than 100 years, damage accidents caused by fatigue still continue even today. While this is indicative of the complexity of the phenomenon called "fatigue," at the same time, it also means that many unsolved problems remain in the field of fatigue. One of those unsolved problems is the problem of gigacycle fatigue, which is the subject of this research.

Normally, steel has a fatigue limit, which is the limit of stress at which fatigue fracture will not occur, and it can be said that techniques for predicting the fatigue limit are virtually established. However, there are some metallic materials that have "no" fatigue limit, and even with steel, the fatigue limit disappears in high strength steels. In particular, in the case of high strength steels, the fatigue limit disappears due to the appearance of internal fracture morphologies that are different from the ordinary fracture mode.

When a fatigue limit exists, a fatigue test on the order of $10^7$ cycles is adequate, but when a material has no fatigue limit, it is necessary to perform the test to the gigacycle region exceeding $10^9$ cycles. However, gigacycle testing is not easy, as the fatigue test can require from several months to several years. This is the problem of gigacycle fatigue.

## Toward elucidation of the mechanism of internal fracture through research on gigacycle fatigue

In research on gigacycle fatigue, ultrasonic fatigue testing is an effective tool. Because ultrasonic fatigue testing can realize a test cycle rate of 20kHz, which is more than 200 times faster than the conventional testing, the time required for a $10^9$ cycle test can be shortened to only 1 day. Although it is necessary to be aware of the effect of the cycle rate in ultrasonic fatigue testing, research carried out to date with multiple materials and under multiple conditions has confirmed that this effect is extremely small when the fracture mode is internal fracture (Fig. 1).

Various research results in connection with gigacycle fatigue have already been obtained using ultrasonic fatigue testing. As examples, elucidation of the mean stress effect, elucidation of the size effect, and elucidation of the effect of hydrogen may be mentioned. Those results revealed that the characteristics of internal fracture differ greatly from those of ordinary fatigue. At the same time, the boundary conditions for clarification of the mechanism of internal fatigue were also arranged. Research and development on inclusion inspections using ultrasonic fatigue testing and the development of a high temperature ultrasonic fatigue test device were also carried out, and as a result, a wealth of knowledge and technology in connection with ultrasonic fatigue testing could be obtained.

At present, we are working toward elucidation of the mechanism of internal fatigue based on the results of research to date. In this work, we propose a hypothetical model that can explain internal fracture characteristics that had been clarified to date, and attempt to verify the appropriateness of that model experimentally. The key in this experiment is observation of internal crack propagation behavior. Unlike surface cracks, internal cracks cannot be observed directly. Therefore, we are developing a technique for visualizing the propagation behavior of internal cracks by the beach mark method, in which traces of crack propagation called "beach marks" are left on the fracture surface, as shown in Fig. 2, when load variations are applied during the fatigue test. Thus, the research on internal fracture of high strength steels has succeeded in "bridging the outer moat" and is now preparing to "conquer the main citadel."

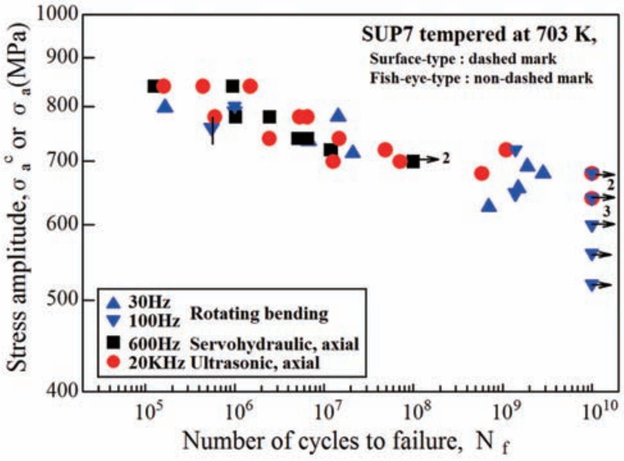


**Fig. 1** Representative examples of ultrasonic fatigue test results.

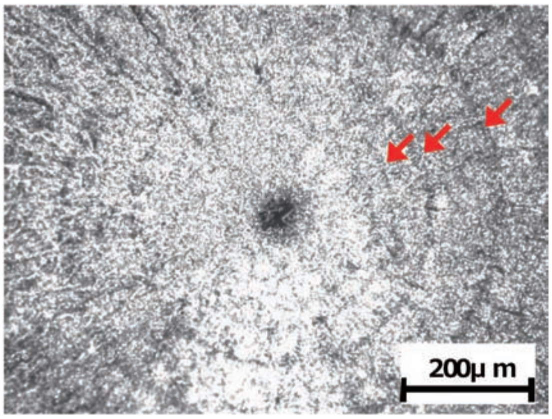


**Fig. 2** Beach marks on an internal fracture surface. The condition of the internal crack when load variations are applied is left on the fracture surface as a ring-shaped pattern.

**Yoshiyuki Furuya** Ph.D. (Engineering) Completed the doctoral course at the Kyushu University Graduate School of Engineering. Joined NRIM in 2000 and became a NIMS Researcher when NRIM was reorganized as NIMS in 2001. Prior to appointment to his present position as NIMS Principal Researcher in 2010, he was a NIMS Senior Researcher in 2005, and was a Visiting Researcher at the Lawrence Berkeley National Laboratory in the United States in 2006. He has been engaged in research on fatigue continuously since joining NIMS. Although the main subject of his research is gigacycle fatigue, his work also includes preparation of data sheets, investigation of accidents, and related activities. While his specialty is dynamics, his background includes research on molecular dynamics (computational) as the topic of his doctoral dissertation, and he possesses a wide range of research experience encompassing both computational and experimental research.

# Fatigue Prediction Technology using Noncontact Ultrasonic Measurement

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Non-Destructive Evaluation Group,
Materials Reliability Unit,
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**Hisashi Yamawaki**

## Crack initiation life

Two approaches are applied to the fatigue life of materials. The first, called "crack initiation life," defines the stage in which a fatigue crack first appears (i.e., "crack initiation") as the fatigue life of a material. The second, "crack propagation life" or "crack growth life," obtains life from the material thickness based on the propagation life of fatigue cracks using test pieces in which an artificial crack called a "notch" is introduced in advance. In recent years, crack propagation life has been used in maintenance control of plants and other steel structures. In this method, the dimensions of cracks are measured by periodic nondestructive inspections, and maintenance is performed based on the results. On the other hand, design based on crack initiation life has been desired for materials used in liquid fuel rocket engines of aerospace and similar applications, as it is impossible to repair these materials while in use. Because no nondestructive method of measuring crack initiation life was available, development of a new technology had been demanded. [1]

## Mechanism of fatigue process and nondestructive measurement – Nonlinear ultrasonic and AE

The mechanism of progress of fatigue cracks in metal materials comprises "dislocation behavior (plastic deformation)" of the origin microstructure which is the microcrack nucleation and its surroundings, initiation and coalescence of microcracks, and propagation of the main crack. For evaluation of crack initiation life, it is necessary to detect the dislocation behavior (plastic deformation) of the microstructure which is the origin of fatigue and its surroundings, and the initiation and coalescence of microcracks.

As a nondestructive measurement technology which is sensitive to dislocation behavior, attention has focused on the nonlinear ultrasonic method, in which harmonic ultrasonic waves are measured. This has been made possible by the development of new wideband sensors in recent years. On the other hand, for initiation and coalescence of microcracks, the noncontact laser acoustic emission (AE) method has been developed and applied to in-situ observation of thermal spraying processes.

## Nonlinear ultrasonic wave and AE in ultrasonic fatigue process in the liquid nitrogen temperature

To date, an ultrasonic fatigue testing machine as a nonlinear ultrasonic measurement method has focused on evaluating the fatigue propagation behavior of high strength steels at room temperature. The technique was developed using a wideband laser vibrometer and continuous waveform recorder and analysis system for nonlinear ultrasonic waves and AE generated during fatigue tests. [2] Based on these results, a nonlinear ultrasonic and AE measurement system for use in ultrasonic fatigue testing in a liquid nitrogen environment was developed for nondestructive evaluation of the crack initiation life of liquid fuel rocket engine parts, which are used in cryogenic environments. [3]

Figure 1 shows the ultrasonic fatigue testing machine, which is housed in a cryostat, the test specimen, and the optical path of the Laser Doppler Vibrometer (LDV). An ultrasonic transducer is located out of the cryostat, and vibration is applied to the specimen via the ultrasonic horn. The vibration of the specimen is measured at the end surface situated at the higher position than liquid nitrogen surface by laser path through a porthole. During ultrasonic vibration, a large amount of mist is generated by vaporization of the liquid nitrogen, cutting off the laser light. A mist shield was provided so that this mist does not block the laser light path.

Figure 2 shows a graph of the cumulative AE hit number detected in the fatigue test and the AE amplitude. Figure 3 is a graph showing the subharmonics, 2nd harmonic, and 3rd harmonic as nonlinear ultrasonic waves detected during the fatigue test.

Because the ultrasonic fatigue testing under low temperature environments is unprecedented method, there are many unknown parts in the physical content of nonlinear ultrasonic wave signal and connection with the AE source.

Nonlinear ultrasonic waves in ultrasonic fatigue testing under low temperature environments show little change in comparison to those at normal temperature, and there are also many unknown points in connection with the AE source. We will continue to focus on this testing method as a new challenge.

1) Mitsuharu Shiwa, Junji Takatsubo, and Eiichi Sato, "Collaboration between NIMS, AIST and JAXA in Non-destructive Reliability Evaluation," Journal of N.D.I. (Journal of the Japanese Society for Non-Destructive Inspection), Vol. 59, No. 10(2010), 492-495.
2) Mitsuharu Shiwa, Yoshiyuki Furuya, Hisashi Yamawaki, Kaita Ito, and Manabu Enoki, "Fatigue Process Evaluation of Ultrasonic Fatigue Testing in High Strength Steel Analyzed by Acoustic Emission and Non-Linear Ultrasonic," Journal of the Japan Institute of Metals, Vol. 73, No. 3, 2009, 205-210.
3) Patent application 2011-228283, "Nondestructive testing and evaluation device for cyrogenic ultrasonic fatigue testing, and analysis and evaluation method," (Mitsuharu Shiwa, Hisashi Yamawaki, Toshio Ogata, Yu Matsuura, Hideki Kobayashi, and Yoshiaki Suzuki).

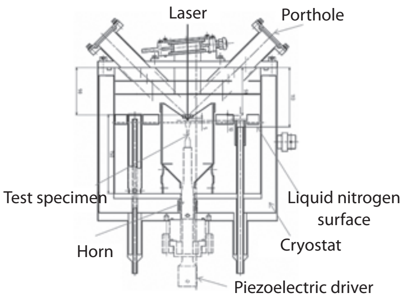


**Fig. 1** Ultrasonic fatigue testing machine for use in liquid nitrogen environment.

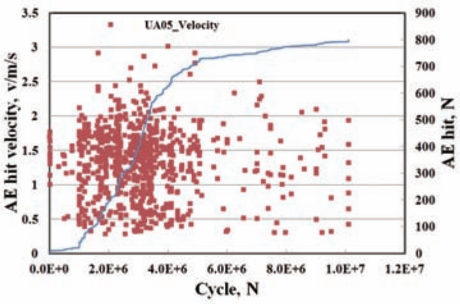


**Fig. 2** AE characteristics during ultrasonic fatigue test.

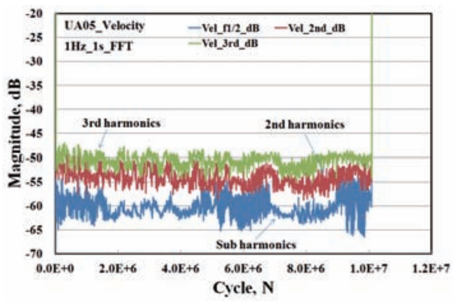


**Fig. 3** Nonlinear ultrasonic waves during ultrasonic fatigue test.

**Mitsuharu Shiwa** Prior to joining NIMS in 2007, he was employed by Nippon Physical Acoustics, the University of Tokyo Research Center for Advanced Science and Technology (RCAST), and the Japan Power Engineering and Inspection Corporation (JAPEIC). His specialty is nondestructive evaluation of materials by electromagnetic, ultrasonic, and AE methods. **/ Hisashi Yamawaki** Joined NRIM in 1980. Since that time, he has been engaged in research on ultrasonic flaw detection, laser ultrasonic wave, computer simulation of ultrasonic waves, and related topics.

# Hydrogen Embrittlement Characteristics of High Strength Steels

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Environment and Energy Materials Division
**Eiji Akiyama**

## What is hydrogen embrittlement?

Hydrogen embrittlement is a phenomenon in which metal materials become brittle when used under load due to the presence of a tiny amount of hydrogen, which can be caused by hydrogen uptake during the material manufacturing process or absorption of hydrogen into the material from the environment. Because fracture occurs with the passage of time, some time after load is applied, this fracture phenomenon is also called "delayed fracture."

In general, the susceptibility of metal materials increases with the strength of the material. Figure 1 shows an example of a high strength bolt in which delayed fracture actually occurred. Today, the development of higher strength materials, beginning with high strength bolts, is being promoted in order to apply higher strength materials to construction, civil engineering, and automotive materials and to utilize hydrogen energy. Thus, as can be seen in the example in Fig. 1, hydrogen embrittlement is a problem that we will inevitably confront accompanying higher strength in materials. This problem has led to renewed and increasing interest in securing the reliability of materials and techniques for their evaluation.

Although various theories have been proposed regarding the mechanism of hydrogen embrittlement, in actuality, debate on this issue is still underway. Thus, elucidation of the mechanism of hydrogen embrittlement and an evaluation method based thereon are expected.

## Characteristics of hydrogen embrittlement

A low speed tensile test was performed with various types of high strength steel notched samples simulating the thread of bolts, when the samples had been charged with hydrogen. The relationship between tensile strength and hydrogen content obtained as a result is shown in Figure 2. It can be understood that the strength of steel materials decreases dramatically even at a trace hydrogen concentration of <0.1ppm (weight ratio). With samples of commercial steels not developed by NIMS, in which the strength level of the commercial steel was changed, it is clear that strength relative to hydrogen concentration decreases as the strength level of the steel increases. Evaluations of the hydrogen embrittlement susceptibility of materials are being performed using this type of test.

## Hydrogen penetration from the environment

For example, in the case of high strength bolts, the source of hydrogen absorption into the material is the corrosion reaction. When metals rust, a reduction reaction inevitably occurs, corresponding to the oxidation reaction of the metal. The reduction reaction involving steel materials, etc. used outdoors is mainly reduction of oxygen. However, partial reduction of hydrogen also occurs. Although most of the resulting hydrogen escapes as hydrogen gas, some of the hydrogen is absorbed into the steel in its atomic form. Under mild conditions, such as atmospheric corrosion, the amount of absorbed hydrogen reaches approximately 0.2 wt. ppm in materials like the commercial steels shown in Fig. 2.

Even though this is a very low concentration, this small amount has a serious effect on high strength steels, as can also be understood from Fig. 2. Accordingly, understanding the process by which hydrogen is absorbed and the amount of hydrogen absorbed accompanying the corrosion process is an important issue.

Figure 3 shows an example of monitoring of the changes in the permeation of hydrogen penetrating steel using electrochemical method in a corrosion test environment simulating atmospheric corrosion. It can be seen that, as the length of the corrosion test increases, hydrogen penetration gradually accelerates. These results suggest that the time required for this acceleration of hydrogen penetration as corrosion progresses is one cause of the delay in delayed fracture.

As hydrogen embrittlement will be an increasingly important issue in the future, we hope to contribute to solving this problem, even if only in part.

**Fig. 1** Example of a bolt that suffered delayed fracture when exposed outdoor in Tsukuba, Japan. Its hydrogen embrittlement susceptibility is increased by increasing the strength of bolts from that of products in practical use.

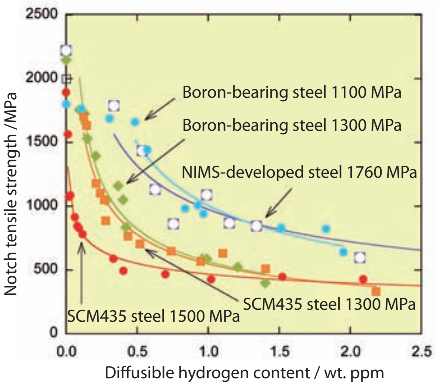


**Fig. 2** Decrease in tensile strength accompanying increased diffusible hydrogen content in various types of high strength steels.

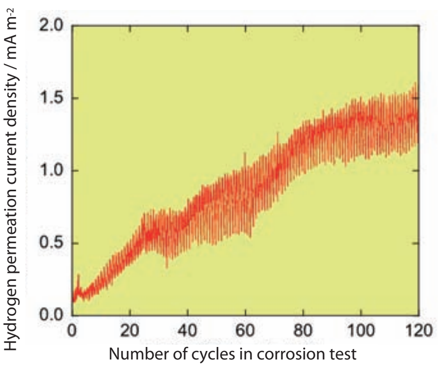


**Fig. 3** Acceleration of hydrogen penetration accompanying progress of corrosion in a cyclical corrosion test.

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# Fatigue Testing under Hydrogen Ion Irradiation Using Cyclotron Accelerator

Environmental Durability Group,
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**Yoshiharu Murase**

## Radiation damage

Nuclear reactor materials are exposed to a special environment which is characterized by a high-energy neutron irradiation field, in addition to simultaneous exposure to the various loads that act on the structural materials in general social infrastructure. In high-energy neutron radiation fields, point defects (displacement cascade damage) such as atomic vacancies and interstitial atoms are introduced into materials due to displacement of the lattice atoms by neutrons. In addition to this displacement cascade damage, new radioactive isotope elements as well as gaseous atoms such as hydrogen and helium are formed (activation) in the material by the nuclear reaction with neutrons (Figure 1).

Displacement cascade damage causes dimensional change and reduced toughness of the material due to formation of radiation-induced defect (RID) clusters through agglomeration of the point defects, while the gaseous atoms formed under neutron irradiation have a remarkable negative effect on the mechanical properties of the material, for example, encouraging embrittlement of the material. These degradations of mechanical properties induced by neutron and other charged particle irradiation environments are generally called as "radiation damages."

## Simulation irradiation tests using a cyclotron accelerator

In research on nuclear reactor materials, most works have dealt with "post-irradiation" experiments using specimens irradiated by neutrons in a nuclear reactor in advance, because the experiments "under-irradiation" in a high-energy neutron field are significantly difficult due to both technical and economical reasons. As a result, understanding of the behavior of materials under irradiation has been greatly delayed. Therefore, we developed an "in-beam" test device (Figure 2) which makes it possible to perform material tests while introducing displacement cascade damage to the specimen using ion irradiation by a cyclotron accelerator. Figure 3 shows the results of a fatigue test under hydrogen ion irradiation using the cyclotron accelerator.

In post-irradiation tests, fatigue testing is performed after first irradiating the specimen with the same amount of radiation dose (= ion beam intensity x time) as in under-irradiation tests. As shown in Figure 3, fatigue life is extended in under-irradiation tests in comparison with non-irradiation and post-irradiation tests. This indicates that the irradiation effect on fatigue behavior under irradiation is larger than that in post-irradiation condition. This enhanced irradiation effect under irradiation is attributed to continuous introduction of RID clusters that act as obstacles to moving dislocations related to fatigue fracture, while RID clusters are consumed and reduced by mutual interaction with moving dislocations in post-irradiation condition.

Thus, this test method adopting another means of irradiation as a substitute for irradiation in a nuclear reactor, is called "simulation radiation testing," and has demonstrated great effectiveness in "mechanism research," to evaluate the actual behavior of materials in reactors by elucidating the mechanism of materials behavior from the data obtained in tests.

## Toward a more advanced "in-beam" irradiation testing technology

Because radiolysis (decomposition under nuclear radiation) causes water to form chemical species that accelerate corrosion, such as $H_2O_2$, it is necessary to perform stress corrosion tests "under irradiation" in order to elucidate the corrosion behavior of nuclear reactor materials. Our aim is to develop an "under-irradiation stress corrosion testing device" as a more advanced version of this "in-beam" irradiation testing technology, and thereby to contribute to further improvement of safety evaluation technology for nuclear reactor materials and high level radioactive waste containment materials.

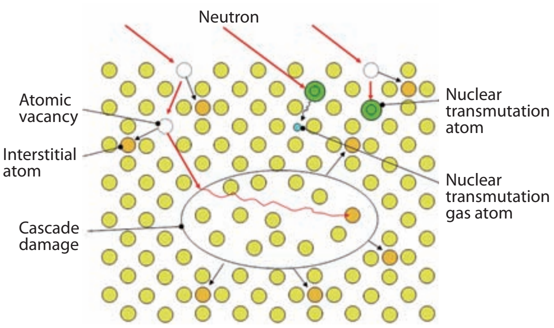


**Fig. 1** Schematic diagram of displacement cascade damage due to neutron irradiation.

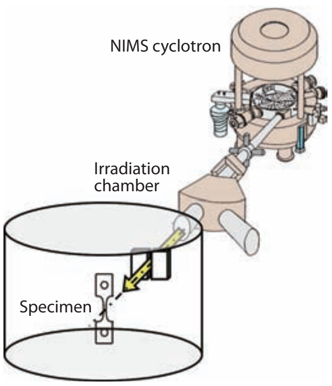


**Fig. 2** Under-irradiation material testing device using cyclotron.

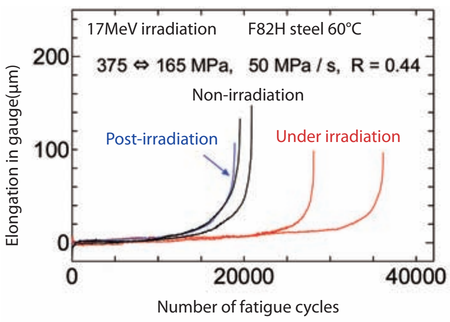


**Fig. 3** Results of fatigue test under hydrogen ion irradiation.

**Yoshiharu Murase** Ph.D. (Engineering) Completed the doctoral course at the Waseda University Graduate School of Science and Engineering and joined NRIM in 1991. He is currently a NIMS Senior Researcher.

# Hierarchical 3D/4D Characterization of Stress Corrosion Cracking

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## Elucidation of the mechanism of stress corrosion cracking of stainless steel

In stainless steel, which is one of the structural materials used in social infrastructure and energy-related equipment, a type of damage called "stress corrosion cracking" (SCC) occurs when external or internal stress is applied to the steel under a corrosion environment. This is a dangerous type of corrosion that may result in a serious accident. In order to prevent stress corrosion cracking, it is important to elucidate the mechanism of SCC crack initiation and growth. In particular, it is necessary to clarify the direction of crack growth and the crack growth rate.

Observation of 2-dimensional cross sections and fracture surfaces has a long history and is widely used. However, this technique cannot clarify the 3-dimensional growth direction and growth rate of cracks. Therefore, this research project is promoting hierarchical 3D/4D analysis of SCC by integrating a variety of analytical methods with unique advantages and features, i.e., X-ray computed tomography (hereinafter, CT), 3-dimensional metallography and micro/mesoscopic strength analysis, and electrochemistry and the acoustic emission (AE) technique, with the aim of elucidating the mechanism of SCC and developing a technology for preventing its occurrence.

## Analysis of SCC using X-ray CT

This section introduces an example of analysis using X-ray CT.

In X-ray CT, 3-dimensional images are obtained by the following measurement principle (Figure 1).
(1) Irradiation of X-rays on a sample, and photography of the transmission image by a detector.
(2) Rotation of the sample, and continuous photography of transmission images.
(3) Overlaying of multiple photographed transmission images by computational processing.

With X-ray CT, it is also possible to reconstruct and output arbitrary tomography images. Figure 2 shows a tomography image of the axial direction of a cylindrically-shaped specimen of SUS304 stainless steel after an SCC test and an image in which the stress corrosion crack is visualized in 3 dimensions. A condition in which the crack has propagated in 3 dimensions from the cylinder surface to the center can be clearly distinguished.

Due to the high atomic density of the main constituent elements of stainless steel, its X-ray transmission capacity is low. For this reason, high brightness radiation sources such as synchrotron radiation have been used until now. Because an X-ray source with high general applicability was used in the present project, it was possible to perform measurements continuously and over a long period of time, which is necessary in order to detect stress corrosion cracking (SCC) cracks that initiate and grow stochastically in stainless steel and to obtain statistical data on those cracks. Moreover, this nondestructive method made it possible to obtain 2D and 3D information more simply than with the conventional technique without destroying the sample. Thus, it can also play the role of a bridge with other analytical techniques.

Based on these results, shortening of the time required for elucidation of the mechanism of SCC initiation and growth is expected.



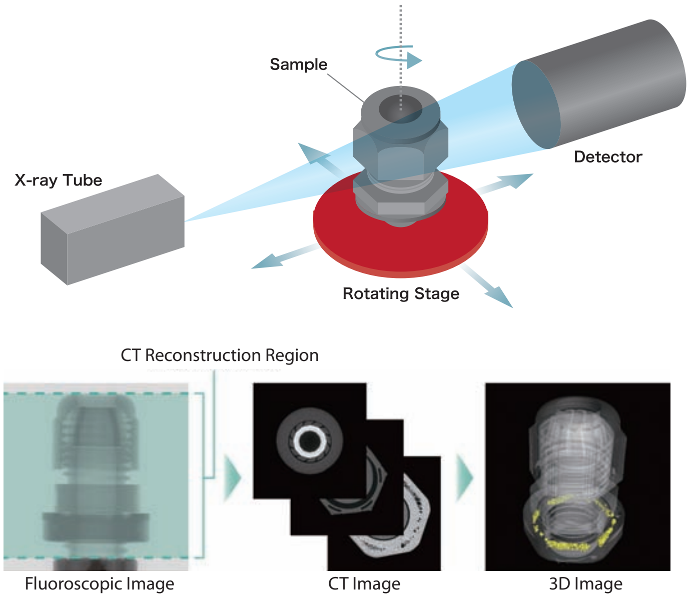



**Fig. 1** Principle of measurement by X-ray CT and the examples of images obtained.

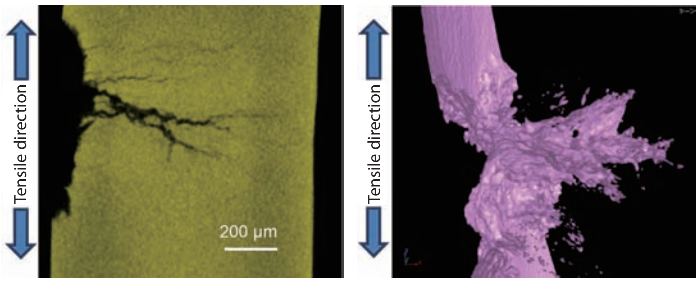



**Fig. 2** Axial tomography image reconstructed and output after X-ray CT measurement of a cylindrical specimen of SUS304 following an SCC test, and an image visualizing the SCC crack.

**Jin Kawakita** Ph.D.(Eng.) Completed the doctoral course at the Keio University Graduate School of Science and Technology and served as an Research Associate at Keio University from 1997. Joined NRIM in 2000, and was appointed to his present position in 2011. During 2004-2005, he was a Ministry of Education, Culture, Sports, Science and Technology (MEXT) Researcher Abroad in the field of nuclear power (Max Planck Institute, Germany) and in 2009, he was a Visiting Research Officer at the MEXT National Institute of Science and Technology Policy (NISTEP). Has held a concurrent position as Professor of the Chiba Institute of Technology Joint Graduate School since 2010. / **Tadashi Shinohara** Ph.D. (Engineering) Completed the doctoral course in Metallurgy and Materials Science at the University of Tokyo Graduate School of Engineering, and then served as a lecturer and an Associate Professor in the Department of Metallurgy and Materials Science, Faculty of Engineering at the University of Tokyo. Dr. Shinohara joined NIMS in 2002. Since 2011, he has been a Visiting Professor of the Faculty of Engineering, Yokohama National University. / **Nobuo Nagashima** Ph.D. (Engineering) Joined NRIM in 1981, and appointed to current position from 2011. / **Mitsuharu Shiwa** Profile can be found on page 6.

Interview

# The Job Doesn't End with Writing a Paper
# How Much Can We Contribute to Society?

**Kazuhiro Kimura,** Unit Director, Materials Reliability Unit, Environment and Energy Materials Division

**Structural materials are the basis of every type of social infrastructure.
The NIMS Materials Reliability Unit is in the forefront of research on reliability evaluation of those materials. In this interview, the Unit Director, Dr. Kazuhiro Kimura, discusses the importance of a social orientation in research, and particularly, an awareness of how one's own research is related to society.**

**—— What do you consider to be the scope of reliability evaluation technology?**

**Kimura(K):** My own field is evaluation technology for high temperature materials. However, as a group, we consider all types of structural materials, in other words, the totality of social infrastructure. Within that broad area, we are putting particular effort into energy-related structural materials.

**—— That is indeed a wide range.
What are you especially mindful of in work on reliability evaluation technology?**

**K:** There is a proverb that says "Persistence will pay off." I think this idea of "persistence," that is, continuing to work patiently with a long-term view of the results, is the most important thing. When someone designs and builds a mechanical structure, it goes without saying that they consider safety, but any material will gradually deteriorate in long-term use. Problems that you don't discover or don't notice in the short term will surface after use for a long period of time. Thus, when thinking about the reliability of materials, it is important to grasp the changes that occur over time. It's too late to make efforts after a problem actually occurs. This means it's important to continue evaluation tests with persistence, anticipating the necessities of the future.

**—— So, pursuing the process is important.**

**K:** Exactly. Naturally, there are also accelerated tests, in which the environmental conditions are deliberately made more severe than the actual use conditions in order to accelerate phenomena that depend on time. However, the mechanism of phenomena that can be induced in a short timeframe is not necessarily the same as the mechanism of phenomena that really occur over an extended time. This is why continuous observation over the long term is so important. For example, in a large-scale project like a nuclear power plant, I think that starting study on evaluation and diagnosis of the deterioration behavior that can possibly occur during operation from design stage, bearing in mind all the processes from design, construction, and operation to decommissioning, is necessary backup for safe and positive introduction of new technology.

In other words, if a reliability evaluation isn't carried out from the point when we ask "what is being made," "what materials are being used," and "how are those materials to be used," it will be too late after problems occur.

**—— Could you comment on how the research system at NIMS has evolved?**

**K:** Ultimately, data sheets are fundamental. We have results of creep tests and fatigue tests that have been conducted over periods of more than 40 years, and we are developing evaluation techniques based on those data sheets, with integration of the data sheets as a first consideration. Of course, the interests of individual researchers are not the purpose of this work. We are constantly thinking about the importance of research as it relates to what materials will be necessary in the future, and what is considered necessary by society. We try to ensure an awareness of how we are related to society in all staff members who are engaged in the testing and research.

**—— What is your dream as a researcher?**

**K:** Perhaps, predicting the process by which structures reach the end of their useful lives by evaluation in as much detail as possible. I think it would be wonderful if we could predict the progress of deterioration using time as a parameter. Also, materials that can be used under more severe environments are generally demanded in order to achieve high performance in equipment. From the viewpoint of responding to the needs of society, I would like to contribute to technological innovation through improvement of the reliability of materials in various environments.

**—— What are your thoughts on today's young researchers?**

**K:** First, the job doesn't end with writing a paper. It is important to ask how much we can contribute to society. These are things that I'm constantly saying. Although we are currently involved in research on 6 subthemes, we are devoting great effort to accurate prediction of how deterioration changes over time, and also to elucidation of the mechanism of why deterioration progresses. Observation and analysis of extremely small regions using advanced nanotechnology is indispensable in research, but because materials are definitely not homogenous substances, it isn't enough simply to observe a small region. From this viewpoint, it's also important to grasp the basic properties of materials by more traditional techniques such as tensile tests and observation of the material microstructure under the optical microscope. N

**Kazuhiro Kimura** Ph.D.(Engineering) Completed the doctoral course at the Graduate School of Tokyo Institute of Technology in 1987, and joined NRIM in the same year. Since 1989, he has participated in the Creep Data Sheet Project, and has been engaged in creep test research. He is now Unit Director of the Materials Reliability Unit of the NIMS Environment and Energy Materials Division.

# Gold Nanoparticles Catalyst Learning from Enzymes in Nature –Metal Nanoparticle Catalyst for Surface Capture of Catalytic Reactants

Group Leader, Functional Heterointerface Group, Polymer Materials Unit
**Kazushi Miki**

Functional Heterointerface Group, Polymer Materials Unit
**Katsuhiro Isozaki**

Functional Heterointerface Group, Polymer Materials Unit
**Tomoya Taguchi**

## A new type of catalyst which mimics enzymes

The new type of catalyst developed in this research mimics a function of natural enzymes. In one enzyme structure, called a metalloenzyme, a metallic element with catalytic activity is located in the active center, and displays extremely high catalytic activity and selectivity by a function in which proteins surrounding the vicinity capture designated substances at active sites.

In this work, we focused on the fact that a self-assembled alkanethiol monolayer formed on the surface of gold nanoparticles has an interaction similar to that of a cell membrane (lipid bilayer), in which designated substances are ingested based on a hydrophilic/hydrophobic phase-separated structure. When molecules are captured on the particle surface by this interaction, it is thought that the catalytic reaction is accelerated due to the higher probability of contact of molecules to the surface of the gold particles that function as the catalyst. In other words, this new catalyst models a metalloenzyme by a material structure of gold nanoparticles coated with alkanethiol molecules NOTE 1 (Fig. 1a, Fig. 1b). This makes it possible to realize catalytic activity similar to that of metalloenzymes. Concretely, we demonstrated a high activity in catalytic reaction, in which silane molecules are activated efficiently at the surface of the gold catalyst by capture of silane molecules and alcohol molecules on the surface of the gold particles.

## Expectations for high activity, high selectivity of catalysts by design of modified molecules surrounding gold nanoparticles.

Figure 1 shows the mechanism of the new catalyst. Modified molecules (thiol molecules) create hydrophobic spaces, which resemble a lipid bilayer, on the surface of the gold nanoparticles (Fig. 1c, left). Silane molecules and alcohol molecules of a designated length and shape are captured, or "encapsulated" in these spaces (Fig. 1c, middle), and the catalytic efficiency of the alcoholysis reaction is greatly enhanced by their proximity to the surface of the gold catalyst (Fig. 1c, right).

In study of the function by which the new catalyst recognizes a designated substance, experiments using carbon chains of various lengths in the alkanethiol and alcohol molecules on the catalyst surface revealed that the highest catalytic efficiency is achieved with a designated combination (Fig. 2). Various verification experiments confirmed that the mechanism of the catalytic reaction is similar to that of metalloenzymes[1)]. In other words, realization of high activity, high selectivity of catalysts can be expected by appropriate design of the modified molecules of the gold nanoparticles.

Furthermore, unlike natural enzymes, which can only be used stably in aqueous solutions, the gold nanoparticles possess extremely high chemical stability. This means that the new catalyst can also be used under acidic, basic aqueous solution conditions and in organic solvents. Therefore, there are no restrictions on industrial applications.

In this verification work, gold nanoparticles surface-modified with thiol molecules were arranged on the surface of a gold thin film and used as a heterogeneous catalyst without dissolution of the solid phase. As catalytic activity, the number of times that a reaction product is formed using atomic gold as a catalyst is expressed by (mol number of product) / (mol number of catalyst). This "turnover" is 200,000, or when expressed as turnover per unit of time, 55,000/hr, which is more than 10 times higher than the turnover of commercial gold colloid catalysts.

This result is the first example confirming a catalytic function of gold nanoparticles modified with alkanethiol. This suggests that it will also be possible to realize the selective capture function of metalloenzyme catalysts for designated molecules by applying ingenuity to the structural design of the alkanethiol molecules.

It should be noted that the precious metal (gold) used in the metalloenzyme catalyst demonstrated in this research could be used without loss because it was immobilized on the substrate without mixing in a solution. Since gold is not only a noble metal, but is also an important industrial resource, this waste-free catalytic structure is considered to be important from the viewpoint of element strategy.

1) Tomoya Taguchi, Katsuhiro Isozaki, and Kazushi Miki Advanced Materials, 24, 6462–6467 (2012).

NOTE 1 Alkanethiol is a substance having a hydrogen atom at one end of a chain-like molecule directly linked to $CH_2$, and a thiol group (hydrogen atom and sulfur atom) at the other end.

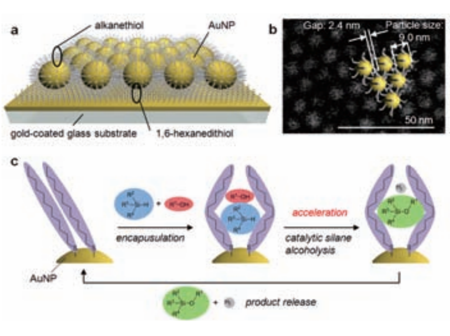



**Fig. 1** Schematic diagram of the new catalyst. **(a)** Catalyst structure, showing the arrangement of gold nanoparticles (AuNP) surface-modified with thiol molecules, **(b)** scanning electron microscope image of the arrangement of AuNP, and **(c)** mechanism by which silane molecules and alcohol molecules are captured by the thiol molecules on the AuNP surface, and catalytic activity is accelerated by proximity to the Au surface.

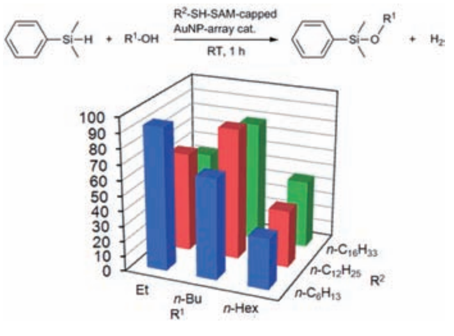



**Fig. 2** Features of reactant recognition by the new catalyst. The new catalyst has the function of recognizing the length and size of reactants, which is similar to the function of proteins. Reactants with a length approximately the same as that of the alkanethiol on the catalyst surface show the highest activity.

**Kazushi Miki** (photo) Ph.D. in Engineering. Completed the Doctoral Program in Engineering at the University of Tsukuba Graduate School.. He joined the former Electrotechnical Laboratory, Japan (now National Institute of Advanced Industrial Science and Technology) as a Researcher in 1987 and was appointed Senior Researcher in 1991. He was a Visiting Researcher at the University of Oxford from 1994 to 1996, and joined NIMS as a Senior Researcher in 2001. He is in his present position since 2003. / **Katsuhiro Isozaki** Ph.D. (Engineering) Completed the doctoral course at the Osaka University Graduate School of Engineering Science. Joined NIMS as a Doctoral Researcher (engaged in this research) in 2007, and moved to the Institute for Chemical Research, Kyoto University as a Program-specific Assistant Professor in June 2012. / **Tomoya Taguchi** M.Sc. (Engineering) Currently enrolled in the Doctoral Program in Materials Science and Engineering, Graduate School of Pure and Applied Sciences, University of Tsukuba (D3).

# NIMS NEWS

## 1 NIMS-NSC-NTU Joint Workshop and Conclusion of Cooperative Graduate School Agreement with NTU and Memorandum of Understanding with NSC

(Jan.10-11, 2013) NIMS, Taiwan's National Science Council (NSC), and National Taiwan University (NTU) held a joint workshop on advanced materials at the NTU campus in Taipei, Taiwan. A total of 13 persons from NIMS, including Prof. Sukekatsu Ushioda, President of NIMS, and Dr. Masakazu Aono, Director-General of the NIMS International Center for Materials Nanoarchitectonics (MANA), participated. More than 20 persons participated from the Taiwanese side, including invited speakers from the four leading national universities, Tsing Hua University, Chiao Tung University, Sun Yat-Sen University, and Cheng Kung University, as well as the NTU.

The workshop began with the signing ceremony for a Cooperative Graduate School Agreement by President Ushioda of NIMS and Prof. Si-Chen Lee, President of the NTU. Following the workshop, President Ushioda and the Deputy Minister of the NSC, Prof. Chung-Yuan Mou signed for a general Memorandum of Understanding, MOU (Comprehensive Collaborative Agreement: CCA) at the Headquaters of the NSC.

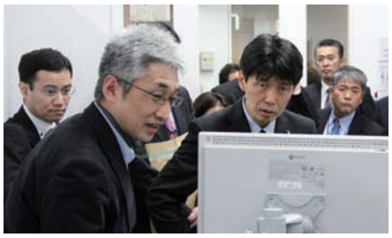
NIMS had previously concluded a CCA with the NTU on February 7, 2012. The launch of the new Cooperative Graduate School system is expected to greatly enhance exchanges with that institution, not only at the faculty level, but also including young graduate students.

NIMS delegates, organizers from the NTU side, and distinguished guests.

## 2 Minister of State for Science and Technology Policy, Visits NIMS

(Jan.9, 2013) Mr. Ichita Yamamoto, Minister of State for Science and Technology Policy visited NIMS on January 9. After arriving at the new building of NanoGREEN/WPI-MANA at Namiki-site, Minister Yamamoto heard a general explanation of NIMS. He then received an overview of the TIA Nano-GREEN project, and expressed his view that "use of superior technological capabilities in business is increasingly demanded." This was followed by demonstrations on sialon phosphors, which the Minister also watched with great interest, after which he toured the NanoGREEN/WPI-MANA Building and inspected a 3-dimensional multi-scale microstructure analysis system (Focused Ion Beam-Scanning Electron Microscope: FIB-SEM) which NIMS developed jointly with a scientific instrument manufacturer.

Minister Yamamoto receiving a general explanation.



Inspection of research facilities.

## Hello from NIMS

**Dear NIMS NOW readers,**

I came to Japan and to NIMS in 2000 right after getting my PhD from Moscow State University in Solid State Chemistry. I applied for postdoc positions in different countries. Japan was the first to reply positively (through the STA Fellowship). This is why I came to Japan, and this choice determined my fate and future. In Tsukuba, I met my wife, and two our daughters were born in Tsukuba. In 2002-2004, I worked in Institute for Chemical Research at Kyoto University. But from 2004, I am in NIMS again, first as an ICYS Fellow and then as a permanent researcher.

On Mount Tsukuba during plum (ume) blossom season.

I enjoyed my research work in NIMS all the time. I could realize my own ideas, use excellent and first-class equipment and facilities, and communicate and collaborate with many brilliant researchers.

When we lived in Kyoto we had possibilities to explore the surrounding nice, famous, and crowded areas in details in all seasons. We admired sceneries and shrines during cherry blossom, fall of the leaves, and even snow. On the other hand, Tsukuba is a quiet town with a lot of parks, a nice place to live with children. When we are tired of our quiet life we can visit crowded Tokyo, and love quiet Tsukuba again.

Why not trying to live and work in Japan, in Tsukuba and NIMS? May be your visit will also change your fate and future.

Typical holiday with children in Doho park.

**Alexei Belik** (Russia)
from 2000-present
MANA Independent Scientist, MANA

NIMS NOW International 2013 vol.11 No.1
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cover image: creep testing machines

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