

Synthesiology

English edition

**Development of regenerative medical technology
working toward practical application**

**Development of highly-active hydrodesulfurization
catalyst for sulfur-free diesel production**

**Development of massive synthesis method of organic
nanotube toward practical use**

**Development of flexible-printable device processing
technology**

A new density standard replaced from water

**A rationalization guideline for the utilization of energy and
resources considering total manufacturing processes**

Synthesiology editorial board

MESSAGES FROM THE EDITORIAL BOARD

There has been a wide gap between science and society. The last three hundred years of the history of modern science indicates to us that many research results disappeared or took a long time to become useful to society. Due to the difficulties of bridging this gap, it has been recently called the valley of death or the nightmare stage (Note 1). Rather than passively waiting, therefore, researchers and engineers who understand the potential of the research should be active.

To bridge the gap, technology integration (i.e. Type 2 Basic Research – Note 2) of scientific findings for utilizing them in society, in addition to analytical research, has been one of the wheels of progress (i.e. Full Research – Note 3). Traditional journals, have been collecting much analytical type knowledge that is factual knowledge and establishing many scientific disciplines (i.e. Type 1 Basic Research – Note 4). Technology integration research activities, on the other hand, have been kept as personal know-how. They have not been formalized as universal knowledge of what ought to be done.

As there must be common theories, principles, and practices in the methodologies of technology integration, we regard it as basic research. This is the reason why we have decided to publish “*Synthesiology*”, a new academic journal. *Synthesiology* is a coined word combining “synthesis” and “ology”. Synthesis which has its origin in Greek means integration. Ology is a suffix attached to scientific disciplines.

Each paper in this journal will present scenarios selected for their societal value, identify elemental knowledge and/or technologies to be integrated, and describe the procedures and processes to achieve this goal. Through the publishing of papers in this journal, researchers and engineers can enhance the transformation of scientific outputs into the societal prosperity and make technical contributions to sustainable development. Efforts such as this will serve to increase the significance of research activities to society.

We look forward to your active contributions of papers on technology integration to the journal.

Addendum to Synthesiology-English edition,

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Synthesiology Editorial Board

Note 1 : The period was named “nightmare stage” by Hiroyuki Yoshikawa, President of AIST, and historical scientist Joseph Hatvany. The “valley of death” was by Vernon Ehlers in 1998 when he was Vice Chairman of US Congress, Science and Technology Committee. Lewis Branscomb, Professor emeritus of Harvard University, called this gap as “Darwinian sea” where natural selection takes place.

Note 2 : Type 2 Basic Research

This is a research type where various known and new knowledge is combined and integrated in order to achieve the specific goal that has social value. It also includes research activities that develop common theories or principles in technology integration.

Note 3 : Full Research

This is a type of research where the theme is placed within a scenario of future society, and where a framework is developed in which researchers from a wide range of research fields can participate in studying actual issues. This research is done continuously and concurrently from Type 1 Basic Research (Note 3) to Product Realization Research (Note 5), centered by Type 2 Basic Research (Note 4).

Note 4 : Type 1 Basic Research

This is an analytical research type where unknown phenomena are analyzed, by observation, experimentation, and theoretical calculation, to establish universal principles and theories.

Note 5 : Product Realization Research

This is a type of research where the results and knowledge from Type 1 Basic Research and Type 2 Basic Research are applied to embody the use of a new technology in society.

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Development of regenerative medical technology working toward practical application

— Construction of human cell processing system in view of safety for the purpose of clinical application —

Hajime Ohgushi

[Translation from *Synthesiology*, Vol.1, No.3, p.170-175 (2008)]

Recently, technology of regenerative medicine which utilizes cells after their proliferation and differentiation process has drawn attention. In order to utilize the technology for clinical application, safety issue of the process as well as usefulness of the cells should be confirmed. We analyzed the issues and succeeded in utilizing the cells after proliferation / differentiation process for the purpose of therapeutic applications.

Keywords : Regenerative medicine, cell culture (cell cultivation), cell differentiation, biomaterial, international standard

1 Introduction

With the recent advances in life science technology, application of advanced medical technology enables revolutionary treatment of diseases for which cure was not available. Advanced medical technology makes new treatment a reality even for serious disease where only option for cure was organ or tissue transplantation. For example, treatments for various intractable diseases are being attempted by regenerative medicine using cells. In regenerative medicine, harvested cells normally require the processes of growing (proliferation) and processing (differentiation) by culture. Needless to say, there must be no contamination by bacteria, mold, or virus in the culture process. Moreover, it is mandatory to ensure safety and efficacy of proliferated and differentiated cells in addition to preventing contamination. Various kinds of cells are used in regenerative medicine, and some are at the stage of practical use along with various risks, from basic research using ES cells to treatment using patient's own somatic cells. Recently in news is the possibility of using induced pluripotent stem cells (iPS) developed by Professor Yamanaka *et al* of Kyoto University instead of ES cells which have ethical issues. However, currently both ES and iPS cells cause tumor called teratoma, and their safeties have not been established and therefore they cannot be used in actual treatment. Considering the above background, this paper reviews the issues in development of regenerative medical technology. Also, to promote early clinical application, we established a medical system for bone regeneration technology that can be readily accepted in the society. I shall describe our approach and results.

2 Issues in the development of regenerative medical technology

Regenerative medicine is a branch of medicine specializing in repairing and regenerating the functions of organs or tissues that were lost by disease or injury, through transplantation of cells or tissue derived from cells. Unlike conventional treatment, it involves the processes of growing (proliferation) and processing (differentiation) cells by engineering techniques for cultivation. Therefore, it is necessary to ensure safety in the processes of cell selection and cultivation. For example, for growing human (mammal) cells, cells are cultivated in culture medium containing various amino acids and vitamins. However, if the culture is contaminated by just one bacterium, since the growth rate of bacteria is several times faster than human cells, there will be far more bacteria by the time human cells have grown sufficiently. Infection may occur when such cultured cells are transplanted to the patient. To prevent such infection, cultivation must be conducted in strictly controlled, bacteria-free environment, or cell processing center (CPC) that specializes in growing human cell (Figure 1).

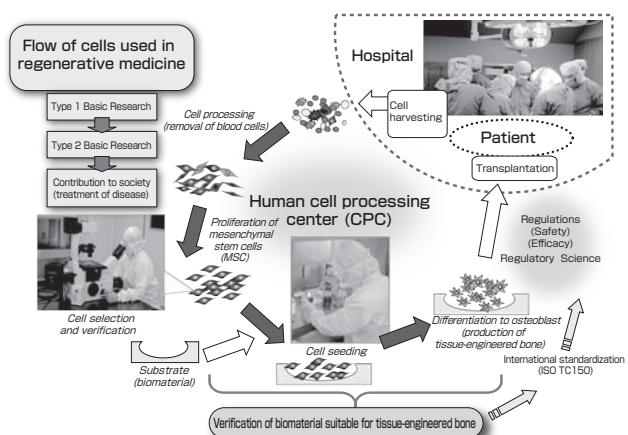


Fig. 1 From culture to transplantation of patient cell.

While growing and processing cells are conducted in CPC, cells that were harvested from patients in hospitals contain various cells other than target cells. Target cells must be isolated and then grown. To accomplish this, development of cell selection technique and evaluation of whether the selected cells are growing well is necessary. The grown cells are converted to specialized cells after process of differentiation so they may develop into tissues or organs that must be regenerated. Evaluation of whether the differentiated cells possess ability as specialized cells is also necessary. In some cases the grown cells are transplanted directly to patient, but in many cases (for example, in our work of bone and joint regeneration), cells and biomaterials are combined and this hybrid material is transplanted. In this case, it is also necessary to evaluate safety of the biomaterial used as well as efficacy of the cells, such as whether the material supports cell differentiation. Standardizing these evaluation processes will enable application to greater number of patients, and hence the treatment may be accepted by the society. The above discussion can be summarized into four points.

- 1) Providing environment for cell processing center (CPC)
- 2) Selection of target cell and verification of proliferative ability
- 3) Verification of cell differentiation (verification of biomaterial)
- 4) Standardization of regenerative medicine

3 Our efforts on regenerative medicine issues

3.1 Providing environment for human cell processing center (CPC)

Figure 1 shows the diagram of cultivation process. Cells (bone marrow) are harvested from the patient in hospital. The cells are transported to our CPC where they are grown. Although in some cases the grown cells are directly transplanted, they are differentiated into component cells of tissues or organs after further differentiation process. The differentiated cells are delivered to the hospital and transplanted to the patient in the hospital. Normally, this differentiation process takes place on various biomaterials^[1].

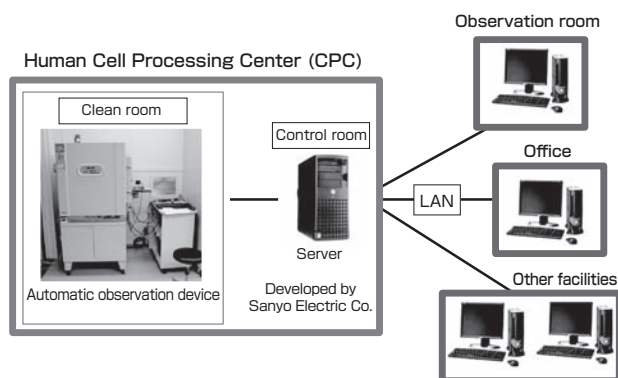


Fig. 2 Providing environment for human cell culture (development of automatic cell observation device).

As mentioned earlier, when bacteria or mold contaminate the culturing processes, bacteria grow along with target cells and the cells become unsuitable for use. Bacteria are present in ordinary environment. Therefore, cell culture maneuvers are conducted in sterile cabinets of the CPC, which is supplied with air from which fine particles are removed by HEPA filter used in clean room in semiconductor plants. Even if sterile environment can be created physically in the CPC, various bacteria exist in human body, and human operator may serve as a source of contamination. However, an operator is absolutely necessary for growing and processing cells in CPC. Also, observation of cell through microscope in the CPC is necessary to check whether the cells are growing and differentiating properly. To minimize entry and exit of operators into the CPC, we developed an automatic cell observation device with Sanyo Electric Co., Ltd.^[2] As shown in Figure 2, using this device, image of any culture dish in any position designated by the user can be observed from remote location via LAN. The cells can be observed without entering the CPC, and sterile environment remains intact. Moreover, culture processing is conducted according to strict quality control procedures, and the work of recording cultured cell data increases the workload of the operator.

Figure 3 shows the images of cell observed at every 24-hour interval using the device. All observations were made for same area (fixed point). The number of cells increases with passage of time, and one can see that the cells are growing properly. There had been no device that allowed remote observation of microscopic field of cell culture at regular time intervals with reproducible results, and thus the significance of this development is high. The device also allows regular recording of observation results as image data. We were able to develop technology that contributes to improvement of quality control and reduction of worker load. Ideally, cell culture that involves no human hands is desirable, and we are working on automatic cultivation device, but I shall not

24-hour interval observation of human cells at fixed-point

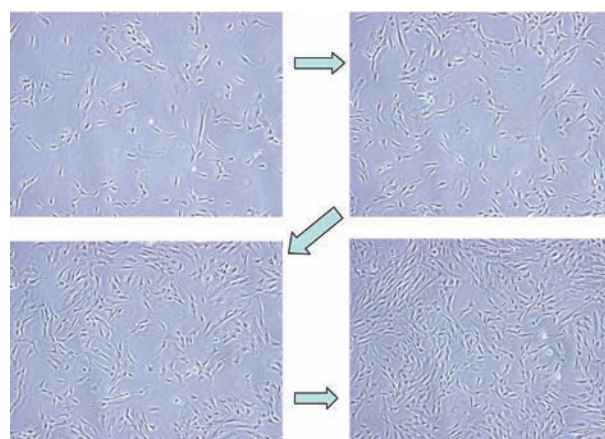


Fig. 3 Fixed-point observation by automatic cell observation device (automatic transportation incubator with cell observation function).

elaborate on this due to space limitation.

3.2 Technology for selecting target cell (verification of cell growth)

Cell growth process is the first process in any regenerative medicine. However, since the harvested cells contain various types of cells, separation of target cell from the mix of cells is necessary. For example, we select and grow mesenchymal stem cell (MSC) from fresh bone marrow that contains hematopoietic cells such as red and white blood cells as well as others. Fresh bone marrow is sowed on culture dish, and the floating blood cells are removed by replacing the culture medium. Thereafter, cells that adhere to the culture surface grow and can be collected. In fact, the cell population collected by this method presents various marker expression usually seen in MSC. However, even at this stage, the cultured cells consists of cell population with different proliferative ability and is not homogenous. This means it is difficult to determine whether the MSC collected at this moment will grow as expected.

In our experience in clinical application, we observed that the growth rate decreases when the nucleus of MSC in culture became thin and the cells flattened in shape. Therefore, we decided to estimate the proliferative ability by measuring this phenomenon quantitatively. We investigated the correlation between the thickness of MSC measured using atomic force microscope and the cell proliferation activity. We found that compared to MSCs with low proliferative ability, the cells with high proliferative ability were smaller and had increased thickness of the nuclear region^[3]. However, the atomic force microscope is extremely expensive, difficult to operate, and takes time to make measurements. Therefore, we worked with Olympus Corporation to investigate whether evaluation of cell proliferation activity level in culture was possible by observing the thickness of area of MSC nucleus and the shape of cell (plane) using light microscope image, and then evaluated cell proliferation activity and developed device to measure proliferative activity using these indices. To measure the thickness of cell by light microscope, the phase

image of MSC that adhered to the culture dish was obtained, and numerical information corresponding to cell thickness and cell surface area were obtained by image processing and analysis software. As shown in Figure 4, the MSC in culture were displayed 3-dimensionally, and the thickness could be measured automatically. Using this device, proliferative ability of the cultured cell could be estimated non-invasively, and it could also check proper growth of the cells. We succeeded in developing technology that allows cell cultivation with higher efficacy. This device can be linked to existing light microscope, and can be accessory device to microscopes that are installed in hospitals and research centers. The device we developed has excellent cost performance, and it is expected that it will be used in various places in the future.

3.3 Verification of cell differentiation (verification of differentiation on material in case cells are hybridized with biomaterials)

In the development of regenerative medical technology, we have worked on the technologies for bone regeneration. Bone regeneration involves the method for regenerative tissue-engineered bone in which MSCs are differentiated into osteoblasts with bone formation ability by cell cultivation, and the bone matrix is formed on biomaterial by these osteoblasts^{[4][5]}. Various types of biomaterials are used to create tissue-engineered bone. Particularly, materials with porous structure to anchor cells are useful. However, evaluation of whether a biomaterial can anchor cells efficiently and whether it has ability to form new bone *in vivo* are necessary. Therefore, we compared the activities of MSC regarding properties of the biomaterial used for tissue-engineered cells, and tried to establish a methodology for assessing new bone formation *in vivo*. To standardize this evaluation method, we employed universal source for cell (in this case bone marrow from rat femur) as well as fixed procedure.

Specific procedures were as follows. Bone marrow of 7-week old rat were cultured in flask to grow MSC, and cell concentration was adjusted to 1×10^6 cell/ml. Porous materials were placed on the culture plate and immersed in adjusted cell suspension. The samples were cultured for 2 weeks using osteogenic culture condition. Detection of differentiated bone cells (osteoblasts) after completion of the culture was conducted by alkaline phosphatase staining. As shown in top photograph of Figure 5, comparing the two materials (porous synthetic hydroxyapatite and hydroxyapatite derived from coral skeleton), bone differentiation was observed only in the pores of surface of the synthetic material. In contrast, cells grew inside the pores in the coral material, and good bone differentiation was observed. The engineered cells were transplanted to rats of same strain. As shown in lower photograph of Figure 5, new bone formation (shown in red) was observed inside the material for coral hydroxyapatite.

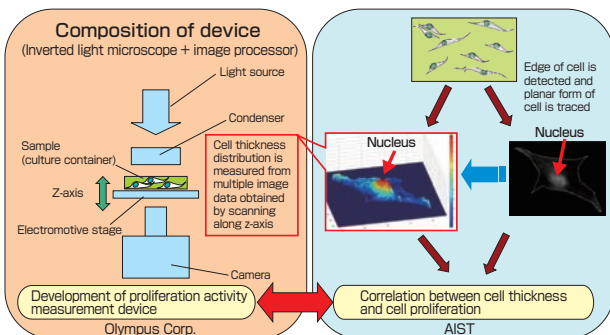


Fig. 4 Development of cell thickness measurement device (evaluation technology for cell proliferation activity and development of the device).

Verification of bone differentiation ability in biomaterial used was accomplished by *in vitro* culture and *in vivo* transplantation. We developed an evaluation technique that allows predictable determination of efficacy of biomaterial used in bone regenerative medicine.

3.4 Standards for regenerative medicine

As described above, in regenerative medicine, it is necessary to constantly verify the efficiency of cultivation process as well as check whether the harvested cells, cultured and grown cells, and differentiated cells are performing properly. Considering commercialization of regenerative medicine, it is mandatory to establish the evaluation method as standards for safety and efficacy of the cells used. The standard for evaluation result is built by employing standardized cell evaluation method, and determination of safety and efficacy can be done readily. Standardization will clarify the indices for increasing efficiency of the process, and this will promote designing and production of regenerative medical products. As mentioned in Section 3.3, we are in the process of establishing the evaluation method of biomaterial used in bone regeneration medicine. Therefore, we are considering international standardization of the evaluation method. Currently, about 230 Technical Committees (TC) are active in the International Organization for Standardization (ISO), and TC150 (Implants for Surgery) is in charge of medical devices. TC150 is further broken down into Subcommittees (SC) and Working Groups (WG) where specialists from around the world engage in discussion. For regenerative medicine, standardization proposal for regenerative medical technologies were discussed in WG11 (Tissue Engineered Implants), and in January 2007, the working group was “promoted” to SC7 (Tissue Engineered Medical Products). We submitted the proposal “*In vivo* bone formation in porous materials using rat mesenchymal cell □ Standardization to evaluate bone forming ability of biomaterials,” to commence activities toward regenerative medical technology standardization originating from Japan. Figure 5 shows the bone formation in the material conducted according to the proposal.

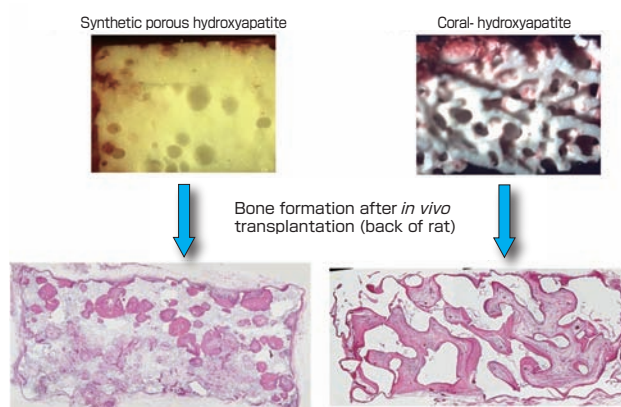


Fig. 5 Verification of biomaterials (areas of osteoblasts location after MSCs seeding).

4 Clinical application of regenerative medical technology

We conducted various technological developments with corporate partners to overcome issues in regenerative medicine. As result, we succeeded in implanting artificial joints formed with tissue-engineered bone to osteoarthritis patient for first time in the world. About 6 years have passed since the first case, and there have been more than 50 cases in total. Although the history is short, there had been no side effects such as inflammation or infection, or “loosening” at the implant site, which is adverse event for artificial joints^[6]. Tissue-engineered bones were also transplanted to cases of bone tumor^[7] as well as arthropathy patients. According to the survey by Fuji Keizai Co., Ltd., there are about 800,000 arthropathy patients in Japan, of which 200,000 patients are estimated to be candidates of regenerative medicine. Our technology is likely to be indicated for many of these patients. Moreover, it was confirmed that MSC could be differentiated into vascular endothelium and cardiac muscle cells^[8], and we started clinical application for heart regeneration in collaboration with the National Cardiovascular Center. As described, we succeeded in developing treatments for heart diseases as well as bone and joint diseases by using cells (bone marrow cells) from patients themselves, and these cells were harvested with minimum invasion (bone marrow aspiration) without sacrificing the patients’ tissues. There are estimated 1,600,000 patients with heart disease. Clinical application to wider range of tissue and organ regeneration can be expected by using the cell differentiation ability of mesenchymal cells from bone marrows to various cells and tissues.

5 Discussion (future issues)

As described above, we developed various technologies for regenerative medicine and have conducted applications or clinical studies in patients with various diseases starting with bone regeneration. However, it is necessary for the companies to spend more effort in medical applications before this technology can benefit patients. The studies must undergo the process of clinical trials, and tissue-engineered cells must be marketed as regenerative medical product after receiving approval of the Ministry of Health, Labour and Welfare. In the United States, Genzyme Corporation markets cultivated chondrocytic (cartilage) cells to over 10,000 patients under approval of the Food and Drug Administration (FDA). In Japan, Professor Ochi of the Hiroshima University conducted 3-dimensional culture of cartilage in collagen gel, and developed the cartilage regeneration technology using this cartilage collagen gel hybrid. This technology was transferred to Japan Tissue Engineering Co., Ltd. (JTEC), and the clinical trials have been almost completed but the product is not yet available. At the same time JTEC started cartilage regeneration, Sewon Cellontech Co., Ltd. of Korea started cartilage regeneration business, received approval of

the Korean Food and Drug Administration (KFDA), and used the product in nearly 3,000 patients.

In skin regeneration, which has longer history than cartilage regeneration, various products are available abroad. However, JTEC only recently obtained approval for regenerative medical product in Japan. The commercialization of regenerative medicine in Japan is obviously slow compared to other countries. The slowness of authorization and approval in Japan is evident. In the future, to promote commercialization of regenerative medicine, the government must work to establish the scientific basis for safety and efficacy of regenerative medical products.

Currently, the Medical Affairs Law regulates the Japanese medical system in business phase. For example, drugs and medical devices must undergo the process of clinical trial as designated by the Medical Affairs Law before they can be marketed. This law is based on assumption that the product will be sold to the general public. However, regenerative medicine where cells are isolated from a patient, cultured and grown, and then transplanted back to the same patient, is a technique in which the patients' own cells (autologous cell) are used. It is medical treatment for specific individual, and therefore, the Pharmaceutical Affairs Law that targets the general public may not be applicable for the treatments. Moreover, in regenerative medicine, the physician must harvest the cells from patient, and one-to-one relationship between physician and patient is established before the actual transplantation of cells, and thorough information are given on the risk and benefit of regenerative treatment using autologous cell before patient's consent is obtained. Regenerative medicine using autologous cell is clearly different from treatment using someone else's (allogenic) cell, and new approval system must be considered for this medical technology^[9]. New system that is not bound by conventional concept must be created to deal with new technological development including regenerative medicine.

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Technology Development Organization (NEDO), as part of Health Program "Development of Evaluation Technology for Early Introduction of Regenerative Medicine."

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Discussion with reviewers

1 Need for technology utilizing MSC

Question (Hiroshi Kuriyama)

I think it is necessary to mention briefly why it is necessary to use patient-derived MSC in the Introduction. I think it is also necessary to describe the danger of iPS cell (as response to common question why iPS, which is frequently highlighted in the media, cannot be used).

Answer (Hajime Ohgushi)

In the Introduction, I added the description that iPS cell may cause tumor called teratoma when it is transplanted.

2 Importance of bone and cartilage treatment

Question (Hiroshi Kuriyama)

Perhaps you should explain how many cases require bone and cartilage regeneration treatment where this technology can be applied, as well as projection of demand in Japan and other

countries in Section 4. Also, I think if you include the numbers of other cases and patients who may benefit from this medical technology, the efficacy of this technological development may become clearer (how about showing the patient figures in table?). Although the data may be available in Reference #6, maybe you should indicate the actual case figures and treatment results for bone and cartilage treatment.

Answer (Hajime Ohgushi)

I added the number of patients with arthropathy and the projected number of patients to whom regenerative medicine may be indicated. I also added the figures for patients with heart disease. The actual number of regenerative treatment for arthropathy that we conducted is 50 or so cases, so I described it as over 50 patients. Detailed description of the treatment result increases the number of words and departs from the main subject, so I simply stated that we have not observed “loosening” at implant site which is adverse event for artificial joint and that good result is maintained.

Development of highly-active hydrodesulfurization catalyst for sulfur-free diesel production

— Full research from in-house laboratory catalyst to commercial catalyst —

Yuji Yoshimura^{*}, Makoto Toba

[Translation from *Synthesiology*, Vol.1, No.3, p.176-182 (2008)]

Clean transportation fuels, particularly with significantly reduced sulfur content, are effective in reducing tailpipe emissions and lead to the development of novel high-performance exhaust treatment devices. We have developed a hydrodesulfurization catalyst for sulfur-free diesel with a sulfur content below 10 ppm as well as a catalyst preparation method, and succeeded in commercializing it as a novel desulfurization catalyst through joint research with a catalyst manufacturer.

Keywords : Sulfur-free diesel, hydrodesulfurization catalyst, catalyst preparation, characterization

1 Background of Research

With enhanced urban air quality control, further reductions are required in tailpipe emissions, particularly nitrogen oxides (NO_x) and particulate matter (PM) emissions from diesel vehicles, and various emission reduction efforts are being made involving improvements to engines, exhaust treatment, and fuels. The first two issues are mainly being addressed by the automotive industry, while the third issue is being addressed by the petroleum refining industry. Exhaust-gas treatment devices include diesel oxidation catalysts, nitrogen oxide removal (deNO_x) catalysts, and diesel particulate filters (DPFs). However, noble metals and basic oxides used as catalysts are susceptible to sulfur poisoning, which can lead to increased fuel consumption due to increased catalyst combustion regeneration frequency. Because of this, sulfur reduction in diesel fuel has been required in order to accelerate the development of innovative exhaust treatment catalysts.

In Japan, the supply of sulfur-free diesel with a sulfur content reduced to below 10 ppm began on a limited scale in 2005 and was subsequently introduced nationwide in 2007. Conventionally, however, the hydrodesulfurization of diesel (sulfur content < 10 ppm) was carried out in an integrated manner through a combination of partial modifications to refinery equipment and the use of a high-performance catalyst, as well as changes in the feedstocks used for hydrotreatment (reduction in hard-to-desulfurize sulfur compounds and nitrogen-rich, high-boiling-point fractions, and reduction in aromatic-compound-rich light-cycle oil (LCO) mixed in), changes in hydrodesulfurization conditions (reduction in oil throughput per unit weight of catalyst), and changes in the hydrodesulfurization process. Consequently,

there are high expectations for replacing the conventional hydrodesulfurization catalysts with high-performance and long-life hydrodesulfurization catalysts that minimize feedstock conditioning and process changes leading to feedstock restrictions and decreased throughput, in order to reduce the production cost of sulfur-free diesel.

The use of sulfur-free diesel is a global trend (Fig. 1). There is rapidly growing demand from overseas refineries for a high-performance hydrodesulfurization catalyst that makes the production of sulfur-free diesel possible without the need to modify existing refinery equipment or change operating conditions when introducing it. Gas oil used in Japan is heavier than that in Europe and the U.S., and contains large amounts of hard-to-desulfurize sulfur compounds. If a hydrodesulfurization catalyst is developed in Japan, this hydrodesulfurization technology has the potential to be used throughout the world. We have therefore been engaged in research and development to commercialize a hydrodesulfurization catalyst for sulfur-free diesel, to meet the social need for clean transportation fuels.

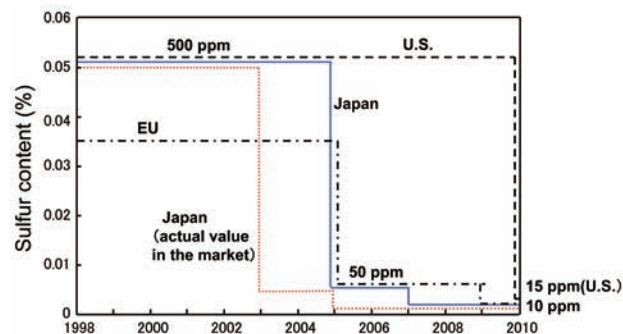


Fig. 1 Trends in diesel sulfur regulation.

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2 Objectives and Outcomes of Research

Diesel fuel is produced by the hydrodesulfurization process in which sulfur (1 to 1.5 wt%) in organic sulfur compounds contained in the gas oil is removed as a hydrogen sulfide by reacting it with hydrogen over a hydrodesulfurization catalyst, thereby converting it to hydrogen sulfide (Fig. 2). With the stringent regulation of sulfur content, the performance of hydrodesulfurization catalysts has gradually improved, resulting in a significant improvement in hydrodesulfurization activity over the past 10 years.

In order to produce sulfur-free diesel under the same conditions as those for producing one-generation-older diesel fuel with a sulfur content below 50 ppm, a highly active catalyst (with about double the activity) is required; in other words, comparable hydrodesulfurization activity can be obtained even at a reaction temperature about 10 °C lower. In the hydrodesulfurization reaction, as the time on stream elapses, the desulfurization activity gradually decreases. Therefore, the quality of the diesel is compensated to ensure a sulfur content below 10 ppm by gradually increasing the reaction temperature; e.g., about 1 °C increase/month. However, carbon deposition on the catalyst surface and structural changes in the catalyst's active components become significant at higher reaction temperatures. Therefore, there are limits to temperature compensation in the high-temperature range. Increasing hydrodesulfurization activity even under lower temperatures is essential for the stable production of sulfur-free diesel (expansion of the temperature compensation range). Hydrodesulfurization catalysts for sulfur-free diesel production have already been developed and commercialized by catalyst manufacturers such as Criterion Catalyst, Haldor Topsøe A/S, and Albemarle Catalyst, as well as oil companies such as Exxon Mobil, IFP/Axens, Cosmo Oil, and Nippon Oil. However, they may be subject to constraints in terms of gas oil types and the operating conditions of hydrodesulfurization facilities. Research and development of high-performance hydrodesulfurization catalysts, i.e., catalysts offering activity enhancement under lower reaction temperatures and longer life, is still ongoing.

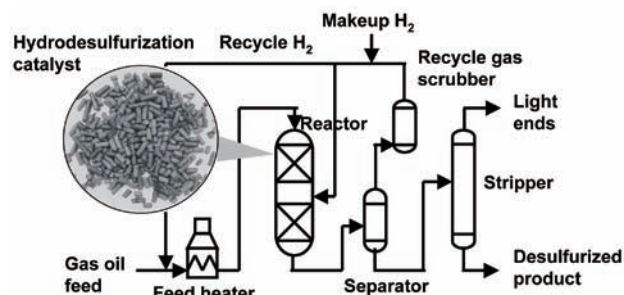


Fig. 2 Schematic diagram of the hydrodesulfurization process in refineries.

We considered that in developing hydrodesulfurization catalysts for sulfur-free diesel, the key to high performance would be the catalyst preparation technology, and conducted full research to refine the developed catalyst preparation technology into “a catalyst preparation technology that can be applied to existing hydrodesulfurization catalyst production lines without the need for modifications.” Specifically, the following research objectives were formulated as representative examples.

Issues related to performance and use of hydrodesulfurization catalysts:

- (1) Hydrodesulfurization catalysts with an activity more than double that of conventional desulfurization catalysts (for diesel with a sulfur content below 50 ppm)
- (2) Hydrodesulfurization catalysts with a lifetime longer than two years (temperature compensation rate for catalyst deactivation: approx. <math><1\text{ }^\circ\text{C}/\text{month}</math>), comparable to that of conventional hydrodesulfurization catalysts
- (3) Desulfurization catalysts with handling characteristics and safety comparable to those of conventional hydrodesulfurization catalysts

Issues related to production of hydrodesulfurization catalysts:

- (4) Upscalable catalyst preparation method (from a beaker scale of a few tens of grams to an industrial scale of tons per day) that can use inexpensive catalyst materials as with conventional hydrodesulfurization catalysts
- (5) Technique to identify and control determining factors in the catalyst preparation process
- (6) Industrial-scale production technology for the developed hydrodesulfurization catalyst

We were not able to address all of the above issues by ourselves, and therefore focused on issues (1), (4), and (5), for which we possess strong research potential. In particular, we focused on issues (4) and (5) involving new preparation methods for hydrodesulfurization catalysts, and jointly developed other items with a catalyst manufacturer.

The research outcomes include the commercialization of a new hydrodesulfurization catalyst for sulfur-free diesel and support for the supply of sulfur-free diesel to the market. The new hydrodesulfurization catalyst can indirectly contribute to the market penetration of diesel vehicles equipped with a high-performance exhaust-gas treatment catalyst. Such a shift to diesel engines can be expected to have a ripple effect leading to CO_2 reduction in the transportation sector.

3 Research Scenario to Achieve the Objectives

As shown by the GC-SCD chromatogram in Fig. 3, obtained by gas chromatography (GC) with sulfur chemiluminescence detector (SCD), gas oil contains various sulfur compounds

such as benzothiophenes and dibenzothiophenes. C-S bonds in these compounds are broken over the sulfide catalyst, and sulfur is removed in the form of hydrogen sulfide (Eq. 1):



This hydrodesulfurization reaction takes place under high-pressure and high-temperature conditions; e.g., a reaction temperature of 330 to 360 °C and a reaction pressure of 3 to 7 MPa. After being loaded with the hydrodesulfurization catalyst, the reactor continues operation for about two years. Most hydrodesulfurization catalysts have metal species (mainly metal oxides) such as Mo, W, Co, and Ni on the surface of porous oxides, and are presulfided before hydrodesulfurization.

The structure of active sites on a hydrodesulfurization catalyst has been a subject of discussion for many years. Today, a structure model is widely supported in which, for example, in the case of a sulfided CoMo-Al₂O₃ catalyst, MoS₂ particles are present on the porous γ-Al₂O₃ support in a highly dispersed state, the Co species is coordinated with the S-edge of the MoS₂ particles, and the Co-Mo-S phase with highly active hydrodesulfurization is formed (Fig. 4).

Topsøe *et al.* [1] classified this Co-Mo-S phase into Type I, which has a significant interaction with the support, and Type II, which has a less significant interaction with the support, and showed that the hydrodesulfurization activity of Type II per unit weight of Co is higher than that of Type I. Consequently, in order to improve the performance of hydrodesulfurization catalysts, a catalyst preparation method was developed to selectively create a Type-II Co-Mo-S structure.

Cosmo Oil [2][3] developed a catalyst preparation method to multilayer the Type-II Co-Mo-S phase (① in Fig. 5: citric acid is used as a chelating agent in the catalyst preparation process). It was found that high activity could be obtained

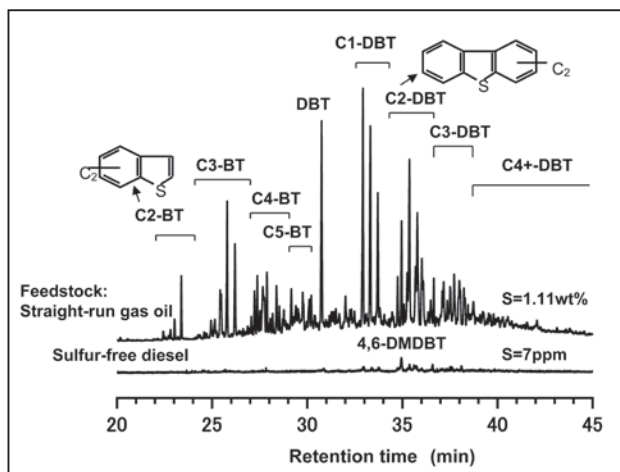


Fig. 3 Sulfur compounds contained in gas oil (straight-run gas oil).

with an average of about 3.8 layers of the MoS₂ phase, and the developed catalyst was commercialized. (It is reported that an alumina support containing zeolite is used as the support for the commercialized catalyst to enhance isomerization activity, in order to avoid steric hindrance by alkyl substituents in sulfur compounds.) AIST [4]-[6] developed a catalyst preparation method to lower the number of stacked layers of the Type-II Co-Mo-S phase (② in Fig. 5). In CoMo/Al₂O₃ or NiMo/Al₂O₃ catalysts used for hydrodesulfurization for an extended period of time, hydrodesulfurization activity is maintained to some extent, but there is lower stacking of layers (mostly single layers) and many MoS₂ particles with the grown (002) face of MoS₂ are present. We therefore considered that they would perform well with lower stacking of layers.

Furthermore, we focused on the crystallinity of the Type-II Co-Mo-S phase with the expectation of the following benefits: (1) As a result of increased crystallinity, the sulfur chemical potential of the catalyst is high and sulfur coordinatively unsaturated sites (hydrodesulfurization active sites) on the Co-Mo-S phase are less susceptible to absorptive inhibition by hydrogen sulfide. (2) The basicity of the coordinated sulfur increases, facilitating its promotion of hydrodesulfurization by removing protons from sulfur compounds and activating hydrogen. (3) Due to the increased

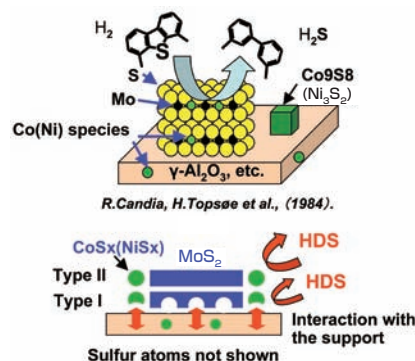


Fig. 4 Model for the active-phase structure of a molybdenum sulfide-based hydrodesulfurization catalyst.

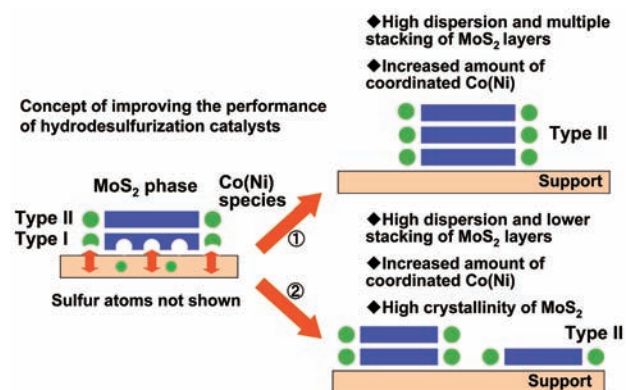


Fig. 5 Approach to high-performance hydrodesulfurization catalysts.

basicity of the coordinated sulfur (reduced Lewis acidity of adjacent sulfur coordinatively unsaturated sites), the hydrodesulfurization reaction is less susceptible to absorptive inhibition by basic aromatic compounds and nitrogen compounds in feedstock oil.

Therefore, we considered that the key to the high dispersion, lower stacking of layers, and high crystallization of MoS₂ and the proper coordination of Co species with the MoS₂ edge sites would be a metal-containing impregnation solution, and focused on establishing the preparation method for such a solution (Fig. 6). The effectiveness of chelating agents (nitrilotriacetic acid, citric acid ^[7], CyDTA ^[8], etc.) in preparing an impregnation solution containing Mopolyanions and Co ions has already been confirmed.

We found a new chelating agent, identified the controlling factors in catalyst preparation, and confirmed that the preparation of highly active Mo-based catalysts is reproducible, although on a laboratory scale.

4 Deepening and Integration of Element Technologies as an Approach

Usually, a catalyst research approach consisting of three parts (a “three-in-one” type of research approach: catalyst design and preparation technique – catalyst structure analysis/evaluation technique – catalytic reaction evaluation technique) as shown in Fig. 7 is used if a proof of principle approach is used for Section 3. This approach is a process in which, as this three-part relationship revolves, the catalyst develops into a high-performance catalyst (evolving in a spiral like a helical spring). It is a series of processes: the latest analytical machines are incorporated to characterize a catalyst that, for example, was trial-produced for specific purposes or purchased on the market; the obtained catalyst structure is correlated to active sites on the catalyst; and design guidelines for an advanced catalyst are proposed.

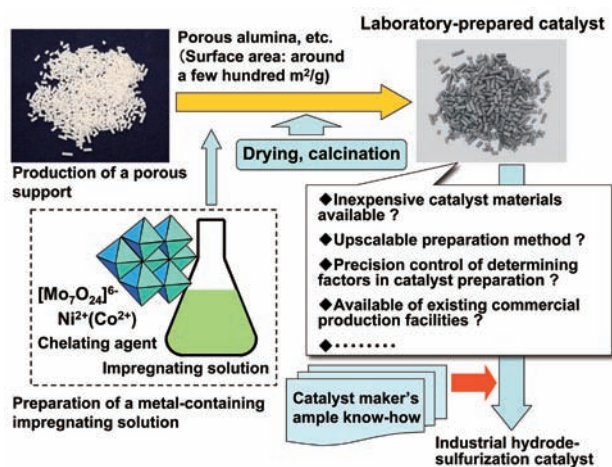


Fig. 6 Catalyst preparation method based on the conventional impregnation method using the new impregnation solution.

With advances in catalyst analysis techniques and theoretical support for catalyst structures (density functional theory (DFT) calculation, etc.), atomic- and molecular-level information on catalysts is constantly updated, and the three-part relationship is evolving and successful. However, for the wet catalyst preparation method, which is the mainstream industrial catalyst preparation method and is widely used for catalyst preparation in the laboratory, information on the prepared catalyst is not necessarily fed back to the preparation stage. This might be due to the limited information available on the properties of metal ions, metal complex, or colloids in the impregnation solutions. It is more appropriate to say that information to help link information on the prepared catalyst to that on catalyst preparation is not disclosed because the preparation process is directly linked to intellectual property. Another feature of this study is that the three-part relationship for solid catalysts, such as preparation of a metal-containing impregnation solution used for catalyst preparation and structural analysis of metal ions in the impregnation solution, was investigated at the solution level, and the catalyst preparation process was reviewed from a chemical as well as engineering perspective.

We assumed that the following were essential to move smoothly from beaker-scale to industrial-scale catalyst production:

- (1) Industrial catalyst materials are inexpensive, the impregnation solution preparation method can correspond to variations in industrial catalyst material lots, and quality control can be applied to a large-scale catalyst preparation process.
- (2) The catalyst preparation method can be used in existing commercial hydrodesulfurization catalyst production facilities.

As a result of studying various aspects, we identified controlling factors in catalyst preparation, although for laboratory preparation; undertook an in-depth study on techniques to control controlling factors; and developed a recipe for catalyst preparation. Subsequently, based on the results obtained at AIST, we conducted joint research with a catalyst manufacturer. It was found that AIST's recipe required improvements, but the overall direction of our

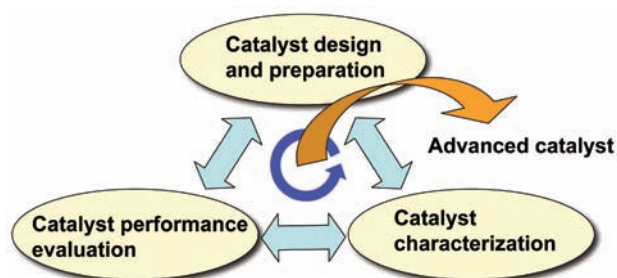


Fig. 7 Three-in-one technology in catalyst development.

research was confirmed to be correct. Through the joint research, we were able to directly learn the requirements for industrial production of catalysts and address them from an academic perspective at AIST. This is probably the foremost reason why it was possible to scale up from the laboratory scale relatively easily.

5 Research Results

5.1 Performance of the Developed Catalyst

The hydrodesulfurization performance of the NiMo/Al₂O₃ catalyst developed by AIST was evaluated under the normal hydrodesulfurization conditions of a refinery (reaction temperature: 340 °C, reaction pressure: 4.9 MPa, LHSV: 1.5 h⁻¹, H₂/Oil feed ratio: 250 NI/l) using a high-pressure continuous-flow reactor. The evaluation showed that sulfur-free diesel (S < 10 ppm, N < 1 ppm) can be produced from straight-run gas oil (S: 1.11 wt%, N: 105 ppm).

5.2 Structural Characteristics of the Developed Catalyst

Figure 8 shows a TEM image of the developed NiMo/Al₂O₃ catalyst (sulfide). The average layer length of MoS₂ particles is about 4.4 nm and the average number of stacked layers is about 1.7. The MoS₂ particles observed by TEM have a smaller basal plane length than a conventional NiMo catalyst and are highly dispersed. The number of stacked layers of MoS₂ particles is smaller than in the conventional NiMo catalyst. Thus, it was confirmed that as initially intended, MoS₂ particles on the γ -Al₂O₃ support were highly dispersed and supported in a lower stacking of layers.

Atomic-level analysis of the MoS₂ phase was conducted through extended X-ray absorption fine structure (EXAFS) analysis of the developed NiMo/Al₂O₃ (sulfide). Figure 9 shows a Fourier transform of the Mo K-edge EXAFS spectra for the conventional NiMo/Al₂O₃ catalyst (conv.) and the developed NiMo/Al₂O₃ catalyst (lab.). The table at top right shows the coordination number, N, of the sulfur atom around the Mo

atom of each catalyst and the interatomic distance, R, of the Mo-S bond, as well as the coordination number, N, of the Mo atom around the Mo atom and the interatomic distance, R, of the Mo-Mo bond, which were obtained by the curve-fitting method. In both catalysts, the interatomic distance of the Mo-S and Mo-Mo bonds was 2.41 and 3.17 Å, respectively, and comparable MoS₂ nanostructures were obtained. In the developed catalyst, however, the coordination number of the Mo-Mo and Mo-S bonds increased. The increase in the former suggests an increased size of the highly crystallized domain in the (002) face of MoS₂. The increase in the latter suggests that the unit cell of MoS₂ is closer to the cell structure of single crystals. The TEM image in Fig. 8 shows that MoS₂ particles have a smaller basal plane size in the developed catalyst than in the conventional catalyst. These findings suggest very high crystallinity (nanocrystal state) of the MoS₂ sheet in the developed NiMo/Al₂O₃ (sulfide), despite the smaller MoS₂ basal plane size. From the above, it was confirmed that as initially intended, MoS₂ particles on the γ -Al₂O₃ support existed in a highly crystalline state.

5.3 Performance of a New Desulfurization Catalyst, LX-NC1

A new hydrodesulfurization catalyst (product name: LX-NC1) was developed by the catalyst manufacturer, with the design concept of improving the functionality of the nanocrystal structure of this low-stacked-layer MoS₂. Figure 10^[9] shows the performance of the developed LX-NC1 NiMo hydrodesulfurization catalyst. In order to produce sulfur-free diesel using existing facilities in refineries, a highly active catalyst with a reaction temperature about 10 °C lower is required rather than a hydrodesulfurization catalyst for producing diesel with a sulfur content below 50 ppm; e.g., CDS-LX6 hydrodesulfurization catalyst, produced by the joint research partner. It was confirmed that the developed LX-NC1 catalyst exhibits high activity at a reaction temperature nearly 17 °C lower, and that sulfur-free diesel can be easily produced.

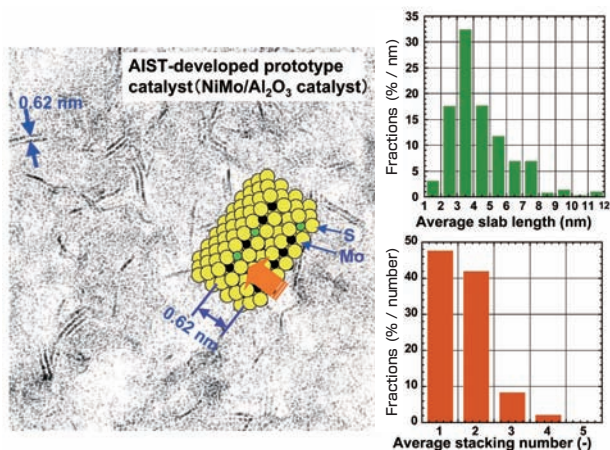


Fig. 8 TEM image of the developed NiMo/Al₂O₃ catalyst (sulfide) and dispersed state of MoS₂ particles.

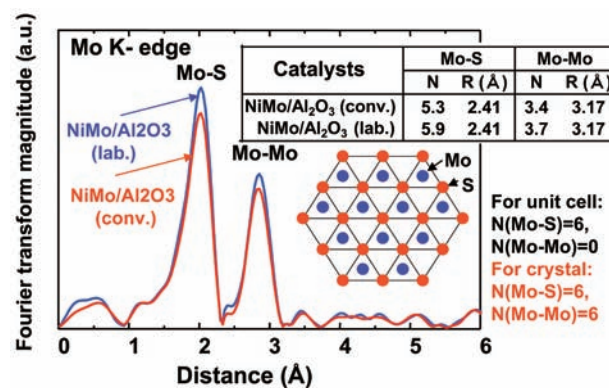


Fig. 9 Local structure of MoS₂ particles on the developed NiMo/Al₂O₃ catalyst.

The stability of activity of the developed catalyst is the most important element of an industrial catalyst. A lifetime test of the developed LX-NC1 catalyst using bench apparatus confirmed very high stability; i.e., during operation to produce diesel with a sulfur content of 7 ppm, the activity reduction rate was less than 1.0 °C/month after a time on stream of two months.

6 Future Plans

The LX-NC1 catalyst for sulfur-free diesel, developed using a new design concept and an advanced catalyst preparation method, can reduce sulfur content from straight-run gas oil both economically and efficiently to produce sulfur-free diesel, and can adequately meet the requirements for sulfur-free diesel production by refineries both in Japan and overseas. It is expected that after the introduction of sulfur-free diesel in Japan and overseas, market introduction of new automotive technologies, including new exhaust post-treatment technologies with the problem of sulfur poisoning mitigated or solved, will be accelerated, resulting in reduced diesel exhaust-gas emissions and improved fuel consumption of diesel engines (reduced CO₂ emissions).

On the other hand, with the stringent regulation of sulfur in gasoline, sulfur-free gasoline was introduced in 2008 in Japan. The sulfur content of premium gasoline had been below 10 ppm, and the issue was to also reduce sulfur in regular gasoline to below 10 ppm.

The main blending stock of regular gasoline is a high-octane gasoline obtained by fluid catalytic cracking of heavy oil, known as FCC gasoline. Most of the sulfur content in regular gasoline comes from FCC gasoline, and hydrodesulfurization technology was therefore required to both reduce sulfur in FCC gasoline and maintain the high octane number. The following hydrodesulfurization processes have been studied: (1) hydrodesulfurization in the fluid catalytic cracking unit;

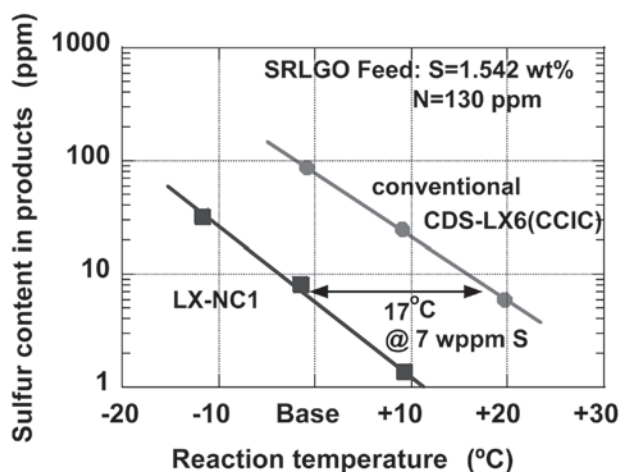


Fig. 10 Hydrodesulfurization performance of the jointly developed LX-NC1 industrial catalyst .

(2) a process in which deep hydrodesulfurization of FCC gasoline is prioritized (simultaneous deep hydrogenation of olefins) and the octane number loss is then compensated for by alkylation, etc.; (3) a selective hydrodesulfurization process in which the hydrogenation of olefins contained in FCC gasoline is minimized (minimization of octane number loss), and thiophenes and thiols are selectively hydrodesulfurized; and (4) an alkylation desulfurization process in which olefins and sulfur compounds contained in FCC gasoline are alkylated and the produced high-boiling-point sulfur compounds are removed by distillation. The hydrodesulfurization processes in (2) and (3) were commercialized. The hydrodesulfurization process in (3) was developed in Japan^[10]. However, a study on the effect of the increased octane number of regular gasoline on fuel consumption improvement has also begun in Japan. The octane number may be increased to around 95 as in the European market (it is currently around 90 in Japan). Demand may therefore increase for hydrodesulfurization catalysts that minimize the hydrogenation of olefins (for example, olefin hydrogenation rate < 15 %) and provide high hydrodesulfurization activity.

In order to improve the hydrodesulfurization selectivity of FCC gasoline, studies are mainly being conducted on the control of hydrogenation of olefins. These include the study of a method of controlling the hydrogenation and isomerization of olefins due to the movement of double bonds in olefins by controlling the acidity of the catalyst support^[10], thereby weakening the adsorption of basic olefins. However, most of the conventional hydrodesulfurization catalysts contain the Type-I Co-Mo-S phase (Fig. 4), and are susceptible to hydrogen activation and the hydrogenation of double bonds even in the presence of hydrogen sulfide. Therefore, there is presumably a limit to control of the hydrogenation of olefins. The hydrodesulfurization selectivity of FCC gasoline is expected to further improve if hydrodesulfurization catalysts contain only the Type-II Co-Mo-S phase (or the Ni-Mo-S phase) and, in addition, if hydrodesulfurization activity per sulfur coordinatively unsaturated site can be improved and the solid acidity of the support can be optimized. In other countries, the sulfur concentration of FCC gasoline is a few hundred to a few thousand ppm (higher by one to two digits than the concentration in Japan), and the need for improved hydrodesulfurization selectivity is higher than in Japan. We plan to apply the preparation method for the developed gas oil hydrodesulfurization catalyst to the production of selective hydrodesulfurization catalysts for FCC gasoline^{[11][12]} to develop applications for the developed technology.

Acknowledgements

The LX-NC1 hydrodesulfurization catalyst for sulfur-free diesel was developed for commercialization through joint research for patent commercialization with Catalysts &

Chemicals Industries Co., Ltd. (currently, JGC Catalysts and Chemicals Ltd.). We would like to thank them. The developed hydrodesulfurization catalyst was the fruit of more than 40 years of research, which was initiated at the former Industrial Laboratory of Tokyo. We would like to thank the senior members of the former institutes, as well as Dr. Akio Nishijima, Mr. Toshio Sato, Dr. Hiromichi Shimada, Dr. Nobuyuki Matsubayashi, and Mr. Motoharu Imamura of the former Nishijima Laboratory.

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Discussions with Reviewers

1 Features of this research

Comment (Koichi Mizuno)

This research work is highly evaluated, since the project is focused on catalyst performance which is one of the factors for improving desulfurization of diesel fuels. However, the desulfurization technologies are wider, and beside catalyst, there are many other improving processes such as distillation of crude oil and so forth. I, therefore, recommend the authors to clarify the potential of technical options of desulfurization processes and to explain the reason(s) for emphasizing the catalyst process.

Based on the above reasons, I felt some narrow viewpoint in the original first manuscript describing "However, since sulfur-free technologies until now has been solved only by replacement of deactivated catalyst with fresh catalyst, higher performance of desulfurization catalysts are highly desired." To make ordinary people understand more easily existing sulfur-free technology (sulfur content <10 ppm), I recommend the authors to describe (1) technological options other than catalyst improvement, (2) disadvantages of the other technologies, and (3) the reason(s) for improving catalyst performance.

Answer (Yuji Yoshimura)

As you have pointed out, in order to produce sulfur-free diesel using an oil refinery facility for producing conventional low-sulfur diesel (sulfur content < 50 ppm), integrated measures are required, including equipment modifications such as the installation of additional reactors, a switch to a high-performance catalyst, the use of an easy-to-desulfurize fraction as the feedstock, the use of reaction conditions to facilitate the hydrodesulfurization reaction, and a change in the blending process for the diesel blending stocks. However, issues arise, such as the increased capital investment cost for revamping facilities and the need for adjustment of the oil product balance due to changes in the feedstock and processes. The switch to a high-performance catalyst is the most economical measure, and

expectations for high-performance catalysts are rising. Therefore, first we have described diesel hydrodesulfurization methods and revised the text to clarify the role of catalyst technology in hydrodesulfurization.

2 Technological goal for gasoline desulfurization

Comment (Koichi Mizuno)

In the Future Plans section, there is a statement that you would like to apply the developed technology to the selective hydrodesulfurization of gasoline. I understand that the target of this statement requires both control of the hydrogenation of olefins as well as improvement of hydrodesulfurization performance. It is not particularly emphasized, however, that catalysts that allow the control of hydrogenation as well as the improvement of hydrodesulfurization have never been explored and are a challenging technology. For the readers' better understanding, I wonder whether you could elaborate on why the technology is challenging and how it can be turned into reality.

Answer (Yuji Yoshimura)

The main blending stock of regular gasoline is high-octane FCC gasoline obtained by the fluid catalytic cracking of heavy oil. Most of the sulfur content in regular gasoline comes from FCC gasoline, and hydrodesulfurization technology is therefore required to both reduce sulfur in FCC gasoline and maintain the high octane number. In order to improve the hydrodesulfurization selectivity of FCC gasoline, studies are mainly being conducted on the control of hydrogenation of olefins. These include the study of a method of controlling the hydrogenation and isomerization of olefins due to the movement of double bonds in olefins by controlling the acidity of the catalyst support^[10], thereby weakening the adsorption of basic olefins. However, most of the conventional desulfurization catalysts contain the Type-I Co-Mo-S phase (Fig. 4), and are susceptible to hydrogen activation and the hydrogenation of double bonds even in the presence of hydrogen sulfide. Therefore, there is presumably a limit to

control of the hydrogenation of olefins. The hydrodesulfurization selectivity of FCC gasoline is expected to further improve if desulfurization catalysts contain only the Type-II Co-Mo-S phase (or the Ni-Mo-S phase) and, in addition, if hydrodesulfurization activity per sulfur coordinatively unsaturated site can be improved and the solid acidity of the support can be optimized. We plan to apply the preparation method for the developed diesel fuel hydrodesulfurization catalyst to the production of selective hydrodesulfurization catalysts for FCC gasoline to develop applications for the developed technology.

3 Future plans for fuel refining technology

Question (Koichi Mizuno)

I understand that the results of your research on catalyst technology are intended to be used for hydrodesulfurizing diesel fuel and will be applied to the desulfurization of gasoline. Do you have a plan to develop other applications?

Answer (Yuji Yoshimura)

There are rapidly increasing expectations for biofuels (in the future, biofuels based on non-food biomass) arising from the need for diversification and secure supply of transportation fuels due to soaring oil prices, as well as compliance with the Kyoto Protocol. Expectations are increasing for new fuel production technologies, including hydrocarbon production using a hydrodeoxygenation catalyst technology, such as from *Jatropha*, a non-food oil crop, and hydrocarbon fuel production using a hydrodeoxygenation catalyst technology for pyrolysis oils (bio-oils) produced by the thermochemical conversion of biomass residue. In these reaction systems, the hydrogenation deoxidation reaction is the main reaction accompanied by the breaking of C-O bonds, unlike the hydrodesulfurization reaction accompanied by the breaking of C-S bonds. These two reactions have a similarity in the mechanism of heteroatom removal over a solid catalyst. We plan to take on the challenge of developing production technology for these new biofuels by improving the developed hydrodesulfurization catalyst.

Development of massive synthesis method of organic nanotube toward practical use

— Integration of molecular design, molecular synthesis and safety assessment for materials having market competitiveness —

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[Translation from *Synthesiology*, Vol.1, No.3, p.183-189 (2008)]

Organic nanotubes are hollow fibers formed through the self-assembly of amphiphilic molecules in a solvent. Because nanoparticles and proteins can be included within their hollow interiors, such nanotubes can be applied to a wide range of fields. To promote the practical use of organic nanotube, we have developed a strategic scenario that fulfills several conditions, including mass synthesis (by integrating molecular design, synthesis, and self-assembly technologies), practical use, low cost, and safety.

Keywords : Organic nanotube, mass synthesis, self-assembly, inclusion, safety assessment

1 Research objective

Organic nanotubes are hollow-fiber substances formed through spontaneous aggregation (or self-assembly) of amphiphilic molecules that feature both water-soluble (hydrophilic) and oil-soluble (hydrophobic) moieties, much like surfactant molecules. Although the sizes of organic nanotubes differ according to the type of molecule used, in general they possess interior diameters of 10-200 nm, exterior diameters of 40-1000 nm, and lengths of up to several hundreds of micrometers^[1].

Amphiphilic molecules have good dispersibility in water because they possess a cylindrically arranged bilayer membrane structure with the hydrophilic parts facing the solvent (Figure 1).

The cyclodextrins, cyclic molecules comprising six to eight glucose molecules arranged in a ring, are used widely in food, drug, and home products. Because various organic low molecular components can be incorporated within the hollow space of a cyclodextrin, unstable substances can be stabilized, drugs and fragrance can be released slowly, and substances that do not dissolve readily in water can be solvated^[2]. The

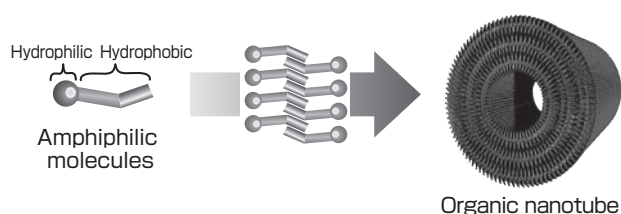


Fig. 1 Schematic representation of the formation of the organic nanotube structure.

hollow space within an organic nanotube is 10 times larger than that within a cyclodextrin; therefore, the former can incorporate large substances, such as proteins, nucleic acids, viruses, and metallic nanoparticles, that do not fit in the cavities of cyclodextrins. In previous studies, we incorporated gold nanoparticles (sizes: 1-20 nm)^{[3][4]} and the spherical protein ferritin (diameter: 12 nm)^[5] into organic nanotubes (Figure 2). Through their development and application in agriculture, foodstuffs, healthcare, medicine, and the environment, we suspect that organic nanotube-based materials will become new, commercially competitive products.

The discoveries of the unique structures and properties of fullerenes (1984), which led to the award of the Nobel Prize in Chemistry in 1996^[6], and carbon nanotubes (1991)^[7] were major nanotechnological breakthroughs; R&D activity continues apace to develop the practical applications of these materials. Notably, although organic nanotubes were developed^{[8]-[10]} in 1984—several years prior to the discovery

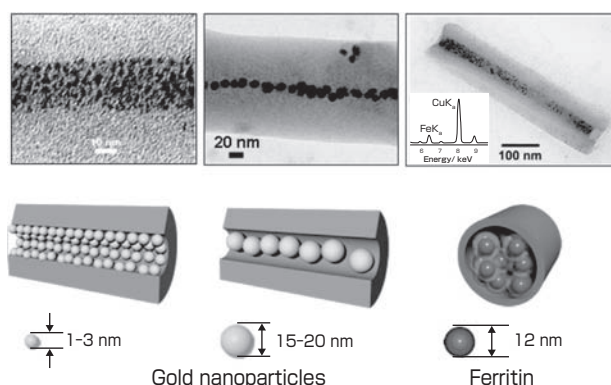


Fig. 2 TEM images displaying the inclusion of (left, middle) gold nanoparticles of various sizes and (right) the spherical protein ferritin within organic nanotubes.

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of carbon nanotubes—they have not been put to practical use, primarily because organic nanotubes have been difficult to mass-produce successfully, unlike carbon nanotubes; therefore, relatively little research has been performed into the practical applications of organic nanotubes or into comparisons with existing materials. Resolving this issue would make it possible to verify the potential of using organic nanotubes as materials for its practical applications.

The objective of this study was to create a new industry involving the practical use of organic nanotubes. To do so, a mandatory requirement was the development of a method for the mass synthesis of organic nanotubes. Also, it was necessary for us to develop low-cost molecules for the synthesis of the organic nanotubes, to perform utilization development, and to demonstrate their safety.

2 Goals and scenario to achieve the goal

For the practical application of organic nanotubes, it is necessary for companies to actually use these materials in trial runs so that they can be accepted as candidates for product development. To promote trial use by companies, it was necessary to develop a mass synthesis method that enables a steady sample supply and provides functions that can be employed in various fields, while fulfilling such practical considerations as cost competitiveness and safety. Thus, it was necessary to determine an optimal molecular structure for organic nanotube synthesis through molecular design and synthesis and then to produce a low-cost molecule by simplifying the synthetic process to cut costs. Also, it was important to lower the entry barrier for industrial use by conducting a safety assessment and sharing the information (Figure 3).

To achieve the aforementioned goals, we first developed a molecular design and synthesis technology using amphiphilic molecules for the fabrication of organic nanotubes with considerations of economy, safety, and mass production. The policy we employed for molecular design was to use a material resource that was recyclable, naturally occurring, and abundant (i.e., available at low cost from a reagent supplier). We established a working hypothesis that amphiphilic molecules synthesized from naturally occurring raw materials would be safe.

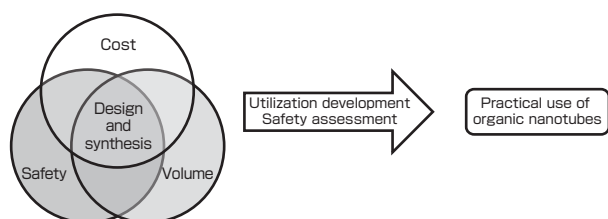


Fig. 3 Schematic representation of the development and application scenario.

Next, we developed a process—an improvement of the established self-assembly method—to enable the mass synthesis of organic nanotubes from amphiphilic molecules. We optimized four phases of the organic nanotube synthesis to increase efficiency and enable mass production: (i) dissolving the amphiphilic molecule in a solvent; (ii) forming organic nanotubes through self-assembly of amphiphilic molecules; (iii) separating the organic nanotubes from the solvent; and (iv) drying the organic nanotubes. Not only would the development of a suitable large-scale synthesis enable both economy and mass production, it would also open up the possibility of developing organic nanotubes in various fields—where investigations have previously been limited by insufficient amounts of materials (e.g., 100 mg or less)^[11]—and enabling appropriate safety assessments.

Third, for the practical application of organic nanotubes in various fields, it was important to recognize their superiority through comparisons with the properties of conventional materials. For utilization development, it is important that companies use the materials in trials to determine whether they can be applied in actual situations. Therefore, it was necessary for us to provide companies developing conventional materials with organic nanotubes and to demonstrate the efficacy of organic nanotubes through joint research opportunities. To encourage the companies to experiment with the materials, we undertook an active promotion campaign, presenting organic nanotube technology at conferences and exhibitions.

Finally, because organic nanotubes are new materials, we knew that they would not be accepted in society unless their safety was established—even if their effectiveness was recognized for utilization development^[12]. Therefore, we conducted safety assessments of the amphiphilic molecules and organic nanotubes that we synthesized from naturally occurring raw materials. We shared this safety information with relevant companies to lower the entry barrier for this technology.

To satisfy the first and second phases of the scenario, it was necessary for us to conduct several tasks simultaneously. Because organic nanotubes exist in the field of supramolecular chemistry, which studies molecules as component units and investigates their assembly functions based on interactions with other molecules, we developed our molecular design, synthesis, and self-assembly methods by carefully investigating the molecular structure and its potential for self-assembly.

The third phase of scenario was to be investigated after completing the first and second phases. Because heteronomous factors had to be solved by comparing the third phase with first and second phases, organized and strategic efforts were necessary for rapid assessment.

The fourth phase was an extremely important aspect of the potential practical application of the organic nanotubes. Although the safety assessment items differed from field to field, we selected common features in the initial phase to motivate the manufacturers to employ our organic nanotubes.

3 Functions to be realized and synthesiological method

3.1 Main elemental technologies

We selected the following five elemental technologies for the practical application of organic nanotubes: (1) technology for the molecular design and synthesis of amphiphilic molecules for the fabrication of organic nanotubes using naturally occurring, recyclable raw materials; (2) technology for the efficient synthesis of organic nanotubes through the self-assembly of amphiphilic molecules; (3) selection of elemental technologies necessary for utilization development; (4) selection and implementation of safety assessment items to widely promote organic nanotubes; and (5) selection of a timely technological transfer policy and appropriate research management for product realization research.

3.2 Integrated system and realized function

Each elemental technology should ideally proceed sequentially, from (1) molecular design and synthesis to (2) self-assembly to (3) utilization development to (4) safety assessment and then to (5) product realization. In actual research, however, things almost never progress in an orderly manner. For the progress of an elemental technology in actual research, planning of the working hypothesis and verification through experiment are repeated between stages (1) and (2). New knowledge is obtained through such repetition (*Type 1 Basic Research*); the research process moves on to stages (3) and (4) when satisfactory answers are obtained. In our R&D study for the practical applications of organic nanotubes, after developing the elemental technology in stage (3), heteronomous factors increased because the process progressed to a phase in which goal achievement became a prime motive (*Type 2 Basic Research*). Specifically, technology was refined further by feedbacks through fusion with conventional technologies to meet demand, comparison with conventional competitive materials, and managerial

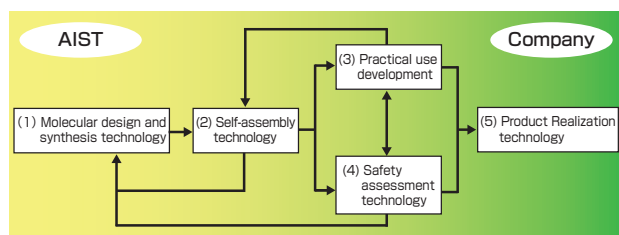


Fig. 4 Conceptual representation of the integration of the main elemental technology for the development and application of organic nanotubes.

decisions (Figure 4). For stage (4), existing information using conventional assessment technologies and comparable assessment methods should be selected at the initial phase because there is very little room for the development of new technology. When utilization development progresses in stage (3) and demand arises in new fields, new safety assessment methods must be developed in stage (4) in collaboration with practitioners in relevant fields.

4 Research results

4.1 Molecular design and synthesis of amphiphilic molecules for the fabrication of organic nanotubes

A few years ago, we discovered a way to selectively form organic nanotubes through self-assembly in water using cardanol/glucose-based amphiphilic molecule 1 synthesized from glucose and cardanol extracted from cashew nut shells.^[13] The characteristic function of this amphiphilic molecule was the selective formation of tubular structures in water; nevertheless, the thermal stability was low, with a gel–liquid crystal phase transition temperature in water of 40 °C. In other words, when the sample was heated to 40 °C, the structure changed from tubes to liposome-like spheres; we determined that we could not put these organic nanotubes to practical use. Therefore, we designed and synthesized the amphiphilic molecule 2, in which hydrogen bonding can occur at the amide group, by replacing the benzene ring linking the glucose unit and the alkylene chain in amphiphilic molecule 1 with an amide unit. As expected, the organic nanotubes created from the amphiphilic molecule 2 was much more heat-stable than molecule 1, with its gel–liquid crystal phase transition temperature being ca. 70 °C^[14]. Although we had solved the issue of thermal stability by using the

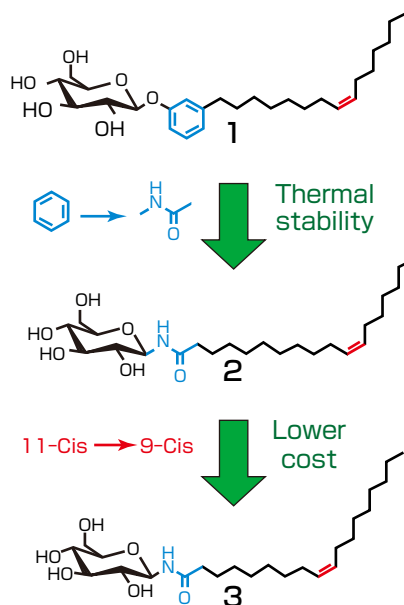


Fig. 5 Molecular design for practical application of amphiphilic molecules.

amphiphilic molecule 2, we departing from our initial plan of using naturally occurring, low-cost materials: the fatty acid raw material for molecule 2, *cis*-11-octadecenoic acid (*cis*-vaccenic acid), was expensive at 30,000 yen per gram. In an attempt to further optimize the molecular structure, we found that *cis*-9-octadecenoic acid (commonly known as oleic acid), which differs from *cis*-vaccenic acid only in the position of its carbon-carbon double bond, was available from olive oil at low cost; gratifyingly, the organic nanotubes synthesized using the amphiphilic molecule 3 incorporating this fatty acid exhibited its gel-liquid crystal phase transition at a temperature of ca. 70 °C, i.e., it exhibited satisfactory thermal stability (Figure 5).

4.2 Self-assembly of organic nanotubes

With the discovery of the amphiphilic molecule 3 that was thermally stable and could be synthesized from naturally occurring, low-cost materials, we set out to investigate an efficient method for the fabrication of organic nanotubes.

In the conventional method, organic nanotubes are obtained after heating amphiphilic molecules in water until they dissolve, waiting until the organic nanotubes had formed through self-assembly in solution and precipitation, and then collecting and drying them. There were three problems with this synthetic method: the solubility of the amphiphilic molecule in water was poor; a long time was required for the organic nanotubes to form through self-assembly in solution; and it was difficult to dry the organic nanotubes collected from the solution.

To overcome these drawbacks, we investigated the self-assembly of this amphiphilic molecule in other solvents. Indeed, we found that using alcohol as the solvent solved each of these problems; i.e., alcohol dissolved the amphiphilic molecules well, the self-assembly progressed rapidly, and the collected organic nanotubes were readily dried^[15].

Using this new synthetic method, we could easily synthesize over 100 g of the organic nanotubes in the laboratory, whereas previously it required much effort to produce 1 g (Figure 6).

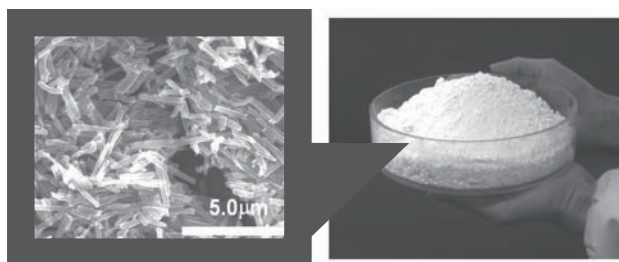


Fig. 6 SEM image (average exterior diameter: 300 nm; average interior diameter: 90 nm) and a photograph of the organic nanotubes prepared in the form of a white solid power (weight: ca. 140 g).

4.3 Utilization development of organic nanotubes

Once we were able to mass-synthesize the organic nanotubes, we conducted a publicity campaign—through press releases and announcements at exhibitions—to attract companies that might have been open to using the material. We made preparations and began to supply samples to various companies in 2007. When providing samples, a material transfer agreement (MTA) was signed between the research institute and each company. The agreement required a specific description of the utilization development and took appropriate measures to understand the fields in which conflicts of interest in intellectual property rights may occur in the future.

As result of sample provision, issues in utilization development for different fields became apparent, and we also found that the time required for practical application differed from field to field. Where practical application could be determined quickly, it was important to optimize supply with demand to enable rapid technological transfer.

For our own utilization development of the organic nanotubes, our research team investigated (a) the preparation of fluorescent organic nanotubes and (b) methods for the decomposition of organic nanotubes under mild conditions, both useful R&D tools in the field of nanobiology, in addition to studying their dispersibility in water and guest inclusion properties.

(a) Development of fluorescent organic nanotubes. This technology involves creating fluorescent organic nanotubes by adding fluorescent molecules during the self-assembly of amphiphilic molecules in organic solution, i.e., during the mass-synthesis of the organic nanotubes (Figure 7). We suspect that these materials will be useful as a research tool for utilization development in the field of nanobiology, where important information can be obtained regarding the stability and behavior of organic nanotubes *in vivo* through observation of cells tagged with fluorescent organic nanotubes.

(b) Method for the decomposition of organic nanotubes. The organic nanotubes form spherical structures when they are heated above their gel-liquid crystal phase transition temperature (ca. 70 °C) in water. While investigating a mild and safe decomposition method, we found that the organic nanotubes transformed into a plate structure when a cyclodextrin solution was added. The tube structure

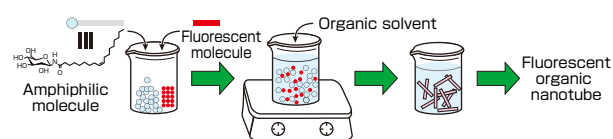


Fig. 7 Cartoon representation of the process used to manufacture fluorescent organic nanotubes.

disassembled when the amphiphilic molecules that comprised the organic nanotubes were included into the cavities of the cyclodextrin (Figure 8). We suspect that the range of applications of these organic nanotubes as functional materials will increase with the discovery of this simple decomposition method performed under mild conditions.

4.4 Safety assessment of organic nanotubes

The safety assessment items for our organic nanotubes were discussed and decided in conference at AIST with departments related to technology transfer, such as the Collaboration Promotion Department, Intellectual Property Department, Technology Licensing Organization, and Technology Information Department.

As result, we conducted four safety tests: (i) biodegradation tests using environmental microorganisms according to “Methods of Testing New Chemical Substances,” Chemical Substance Control Law (CSCL), which is required if materials are to be synthesized at scales greater than 1 ton; (ii) oral acute toxicity tests using rats to meet requirements for use in food and drugs; (iii) ecotoxicity tests to assess the impact on aquatic organisms that are most likely to be influenced by exposure to the substance in the environment; and (iv) reverse mutation tests to assess mutagenicity^{Note 1)}.

In the biodegradation tests using environmental microorganisms, we found that our organic nanotubes had almost no effects on humans, animals, or plants because they were almost completely degraded by environmental microbes within 28 days of release into the environment. In the oral acute toxicity tests, we observed no fatalities in the 2 weeks following oral administration of 5000 mg/kg organic nanotubes to rats. The acute toxicity was extremely low, with a least lethal dose (LDL₀) of 5000 mg/kg or higher for both male and female rats. In the ecotoxicity tests using algae, water flea (*Daphnia magna*), and orange rice fish (*Oryzias latipes*), we tested a 100 mg/L organic nanotube solution for its 72-hour growth inhibition, 48-hour acute mobility inhibition, and 96-hour acute toxicity; we observed no growth inhibition, no mobility inhibition, and no acute toxicity. The reverse mutation test for mutagenicity was negative.

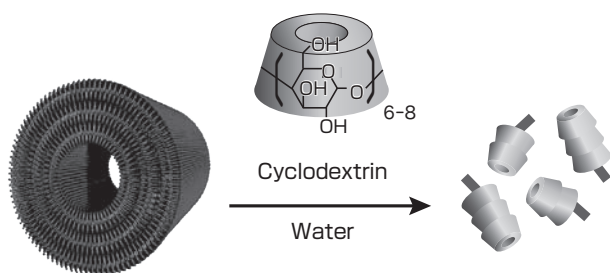


Fig. 8 Decomposition of organic nanotubes through the addition of cyclodextrin.

5 Discussion: Comparison of research results and scenario

By conducting *Type 1 Basic Research* into the development of a molecular design and synthesis technology for amphiphilic molecules that self-assemble into organic nanotubes, we succeeded in designing and synthesizing low-cost amphiphilic molecules using naturally occurring, recyclable raw materials. Moreover, by integrating *Type 1 Basic Research* into the development of a self-assembly technology with this molecular design and synthesis technology, we achieved the mass synthesis of organic nanotubes (*Type 2 Basic Research*). With these results, we enabled R&D into the practical use of these organic nanotubes.

To solve the issues relating to utilization development, we are in the process of providing samples to companies, organizing issues that became apparent through communications with companies, and working on R&D to solve problems. To overcome the unique issues that arise in each field of utilization development, we will continue to cooperate with related fields and companies and develop appropriate research systems.

For safety assessment, we conducted four tests: biodegradation tests using environmental microorganisms, oral acute toxicity tests using rats, ecotoxicity tests to assess the impact on aquatic organisms, and reverse mutation tests to assess mutagenicity. Safety was confirmed in all tests. The results have been regarded highly by many people when we have provided samples to companies; in addition, consideration of safety concerns from an early stage has proven to be useful in lowering the entry barrier to industry. Also, safe use of amphiphilic molecules synthesized from naturally occurring raw materials, as we had hypothesized in the molecular design phase, was proven in this case.

For technological transfer policy, it was difficult for us to set a timeline when creating the schedule and, at present, it remains difficult to provide an optimal solution because so-called people, thing, and money factors are involved, and there are complex time factors that depend on utilization development. In this research subject, as a result of seeking potential applications of our organic nanotubes by transferring the material widely, it became clear that some fields were capable of implementing utilization quickly while others needed considerably more time. Our priority in advancing technological transfer was to optimize supply with demand by extracting R&D elements for fields that could implement utilization most quickly. Moreover, for rapid technological transfer, we decided to establish a joint research system based on a material transfer agreement, developed a system for open-type joint research, and began our own R&D examinations.

6 Future issues

For research into the practical use of organic nanotubes, a new material that has never been used in the world, we selected an open R&D method where utilization development was sought openly through material transfers, rather than a closed R&D method within a research institute, because we expected that applications would be possible in a wide range of fields. This approach became feasible after we had achieved the mass synthesis of organic nanotubes. At the same time, this mass synthesis enabled safety assessments to be performed at early stages of the R&D, enhancing the potential for practical use of our organic nanotubes and helping to raise the awareness and acceptance by companies.

In the future, based on feedback obtained from the companies that accepted our samples, we shall (i) extract elemental technologies for utilization development and investigate solutions and (ii) develop Product Realization Research through collaborations with these companies. Also, we shall seek out fields where markets might form quickly and slowly. In the quick fields, we must prepare a system for supply to meet demand; in the slow fields, we must conduct R&D to accelerate the process through collaborations with universities. In particular, for the creation of a new industry, we must consider the development of new safety assessment methods and industrial standards for organic nanotubes, and we shall continue R&D through collaborations with practitioners in related fields and to collect/accumulate necessary information. Also, based on the concept of minimal manufacturing^{Note 2)}, we shall refine the synthetic method for the preparation of the organic nanotubes and create a new industry through the practical application of organic nanotubes by providing high added value through efficient synthesis, process development, and size control.

Acknowledgements

This study was conducted as part of a joint research project between the AIST and the Japan Science and Technology Agency (JST) through the “Core Research for Evolutional Science and Technology (CREST), 2000~2005” project and the subcontracted “Solution Oriented Research for Science and Technology (SORST), 2005~2008” research project.

Notes

Note 1) Tests were subcontracted to specialized testing organizations; they were conducted according to the following methods:

Biodegradation tests: “Biodegradation Test of Chemical Substance by Microorganism” in *Methods of Testing New Chemical Substances*, CSCL.

Oral acute toxicity tests using rats: “On Guidelines for Single and Multiple Dose Toxicity Test,” appendix to *Guideline for*

Toxicity Test for Drugs and “On Revisions to Guidelines for Single and Multiple Dose Toxicity Test.”

Ecotoxicity tests: For acute toxicity tests of fish, “Fish, Acute Toxicity Test,” *OECD Guideline for Testing of Chemicals 203* (1992); for the sea flea, “*Daphnia* sp., Acute Immobilization Test,” *OECD Guideline for Testing of Chemicals 202* (2004); for algae growth inhibition tests, “Freshwater Algae and Cyanobacteria Growth Inhibition Test,” *OECD Guideline for Testing of Chemicals 201* (2006).

Note 2) National Institute of Advanced Industrial Science and Technology: Part III 3: Nanotechnology, Material, and Manufacturing Fields, Kenkyu Senryaku (Phase 2 Research Strategy 2008). http://www.aist.go.jp/aist_j/information/strategy_revise.html

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Masumi Asakawa

Joined the National Institute of Materials and Chemical Research, AIST, in 1996. Engaged in research on molecular elements and molecular assembly using supramolecular chemistry methods to study assembly function based on molecular interactions. After experiencing major responsibilities as head of the planning section in 2004, started the development and practical applications of the mass synthesis of organic nanotubes. In this paper, worked on the mass synthesis, safety assessment, utilization development, and promotion for practical use, and was in charge of the overall conceptualization.

Masaru Aoyagi

Joined AIST in 2001. Worked on research into molecular recognition (self-assembly, inclusion chemistry) by monomolecular membranes at air-water interface and the development of related sensor systems. Recently worked on refining the organic nanotube synthesis and investigating and assessing phenomena (e.g., adhesion, release) caused by organic nanotubes and other substances. In this paper, worked on developing the synthesis process and practical applications.

Naohiro Kameta

After joining the JST-SORST project, has worked on the development of chemical processes for tailor-made organic nanotubes that can include and release biomacromolecules (e.g., proteins, DNA) upon exterior stimulus. Also working to clarify the properties of nanospace, such as assessing the dynamic behavior and stability of protein inclusion in the cylindrical hollow spaces inside organic nanotubes. In this paper, worked on manufacturing the fluorescent organic nanotubes that may become major tools in the field of nanobiology.

Masaki Kogiso

After joining the National Institute of Materials and Chemical Research, AIST, in 1995, has been working on research into one-dimensional nanostructure formation through self-organization of peptide lipids; i.e., forming nanostructures never seen in the world before, through simple methods, from simple compounds. As result, was the first to mass-produce organic nanotubes, leading to this *full research project* from basic research performed in the laboratory. Currently planning the construction of an organic nanotube library with various surface functional groups using a simple peptide lipid incorporating glycyglycine. In this paper, worked on the development of the mass synthesis and its practical uses.

Mitsutoshi Masuda

After joining the Research Institute for Polymers and Textiles, AIST, in 1992, worked on the functionalization through polymerization and formation of nanofibers and the preparation

of nanofibers through self-organization of, for example, dual-headed glycolipids and aromatic amides. Developed asymmetrical interior/exterior surfaces of organic nanotubes and selective modification of their interior surfaces. Currently planning elemental technology to determine the physical properties and practical applications of nanospaces within organic nanotubes. In this paper, worked on the molecular design and synthesis technology of amphiphilic molecules.

Hiroyuki Minamikawa

After joining the Research Institute for Polymers and Textiles, AIST, in 1988, worked on molecular design and synthesis, lipid molecule assembly, liquid crystal structures, functional analysis, and colloid chemistry using functional lipids (e.g., glycolipids). Currently working on interactions between lipid assemblies and biomacromolecules. In this paper, worked on the structural correlation assessment and property assessment based on the molecular design of the organic nanotubes.

Toshimi Shimizu

Joined the Research Institute for Polymers and Textiles, AIST, in 1977. Head of the Nanoarchitectonics Research Center, AIST, from 2001. Coordinator of the Nanoarchitectonics Research Center from 2008. Worked as a researcher representative of JST-CREST and JST-SORST of the Industrial Science and Technology Frontier Program from 1996, and has made a steady effort to pioneer and develop bottom-up nanotechnology. In this paper, worked as research coordinator for optimizing the molecules for fabricating the organic nanotubes and their nanobiological applications.

Discussion with Reviewers

1 Thinking on the range of R&D that should be done by AIST leadership

Question (Kazuo Igarashi)

Item (5) of Figure 4 is Product Realization technology, but after reading the paper to the end, I see only mention of technological transfer policy for Product Realization. Please explain the positioning of Product Realization as described here and the range of R&D that should be done by AIST as perceived by the Authors.

Answer (Masumi Asakawa)

In Figure 4, the transfer of the contributions from the AIST to the companies is expressed as a color change from yellow to green. We believe that Product Realization in stage (5) should be performed primarily by the companies. Therefore, in this paper, we discuss the need to establish a technological transfer policy and research management system that enables rapid Product Realization by the companies after phases (3) and (4).

Therefore, the issue remains regarding the extent of AIST's involvement in certain phases, but, because we believe that the companies should take initiative in Product Realization, in this paper we describe the phases immediately prior to Product Realization.

2 Measures against nano-risk for organic nanotube

Question (Kazuo Igarashi)

On safety assessment technology in Figure 4, it is written: "Existing information using conventional assessment technologies and comparable assessment methods should be selected at the initial phase because there is very little room for the development of new technology." However, I do not think assessment methods differ by each development phase. Does this mean the level of

evaluations to be done?

Also, in Section 4, you conducted safety tests on rats, and according to the paper, it seemed that the Authors conducted the tests in their own laboratory. There is no problem if this is correct, but if the tests were subcontracted to outside institution, you should state clearly that they were subcontracted. In addition, what is the reliability of the tests?

Answer (Masumi Asakawa)

Safety assessment technologies for nanosized materials, including organic nanotubes, have not been established firmly in every field. While the reactivity and permeability are expected to increase as a result of the nanoscale dimensions, unexpected effects must also be considered. For example, when using a nanomaterial in food or medical fields, while we can expect certain effects that are due to the size, it is necessary to develop assessment technologies to protect against unexpected effects.

Currently, we are working on an investigation system with researchers from the National Agriculture and Food Research Organization. We have also established a new subcommittee, "Food Nanotechnology," in the Materials Forum at AIST to investigate the relationship between food and nanotechnology.

We subcontracted the safety tests to outside institutions, as stated in Note 1. Concerning their reliability, we have added additional information regarding the test methods.

3 Understanding of Type 1 and Type 2 Basic Research and scenario composition

Question (Hisao Ichijo)

I understood that design, synthesis, and structure-function analysis conducted in the early stage of organic nanotube research are *Type 1 Basic Researches*, and "mass synthesis" conducted based on these findings is *Type 2 Basic Research*, but were they positioned as *Type 1 Basic Research*? In Section 2, it is mentioned that working hypothesis and experiments were repeated between (1) and (2), but does this mean that optimal method was found by trial-and-error? Moreover, it is written that utilization development is *Type 2 Basic Research*, and Figure 4

shows it is done mostly by companies. It is described that only the development of Fluorescent organic nanotube is utilization development and no other specific examples are given. Are there other researches?

Answer (Masumi Asakawa)

(1) *Type 1 Basic Research* and positioning:

If it is judged that "mass synthesis" was achieved through the integration of two forms of *Type 1 Basic Research*, namely (i) molecular design and synthesis technology and (ii) self-assembly technology, then I believe that it can be considered as *Type 2 Basic Research*.

(2) Finding optimal method by repeating working hypothesis and experiment, and by trial-and-error:

Yes, the optimal procedures and materials were developed this way. Once the concept and landing point of a research program have been determined, no matter where the starting point is, the landing point is approached using a so-called PDCA (plan-do-check-act) cycle that involves planning out a working hypothesis, doing the experiments to investigate the hypothesis, checking the results, and acting on the issues. The optimal solution for the starting point obtained between stages (1) and (2) will become a greater cycle as it progresses on to stages (3) and (4), and we can bring stage (5) closer to an optimal solution that will satisfy our customers. I believe that how we determine the starting point depends to a great extent on the background of the research conducted so far, as well as on the experience and insight of the researcher.

(3) Other research:

In Figure 4, we present, in a mixture of yellow (AIST) and green (company) hues, how much can be achieved through collaboration of the AIST with external companies for utilization development. Other research includes the development of suitable methods for organic nanotube decomposition through the addition of a cyclodextrin. We have described a specific example.

Development of flexible-printable device processing technology

— For achievement of prosumer electronics —

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We have worked on the development of the flexible-printable device processing technology as a processing technology of information terminal device that can make the best use of user's individuality. We have succeeded in the development of several low-temperature printing technologies for flexible active devices such as flexible displays and circuits. In this research, we have paid attention especially to the social requirements for the technology, and positions of respective technologies in the total set-up concept. We believe that it would contribute to the expansion of information technology in the world.

Keywords : Display, information terminal device, flexible device, process innovation, organic semiconductor, printing

1 Background: flexible information terminal device in demand

As IT technology has deeply penetrated the society today, development of technology that improves usability will diffuse IT technology further and is expected bring forth economic impact. The new technology may also contribute to sustainable society by conserving resource and energy for transportation and communication. The development of technologies for software and hardware for sustainable society is being conducted actively, and the international competition in this field is becoming fierce.

The hardware for IT technology can be roughly divided into “central-mainline technology” where information are collected and processed and “terminal-access technology” where information are received and distributed (Figure 1). The

former, as exemplified by computer, emphasizes “high speed,” “high capacity,” and “standardization,” and various R&D efforts are conducted mainly in silicon technology. On the other hand, the latter, as exemplified by display, emphasizes “diversification,” “mass diffusion,” and “usability,” and there are demands to accommodate various uses and places where the technology is used. For further diffusion and expansion of IT technology, diffusion of information terminal is essential, and creation of more convenient terminal is awaited. To create new information device, it is important to understand the market demand. Particularly, as the general public is becoming accustomed in using the network, demands for usability are increasing. For example, we well as demands for hardware such as being light, thin, or doesn't break when dropped, there are demands for usability such as not being affected by place or environment in which the device is used (everywhere device), or user can customize the device to

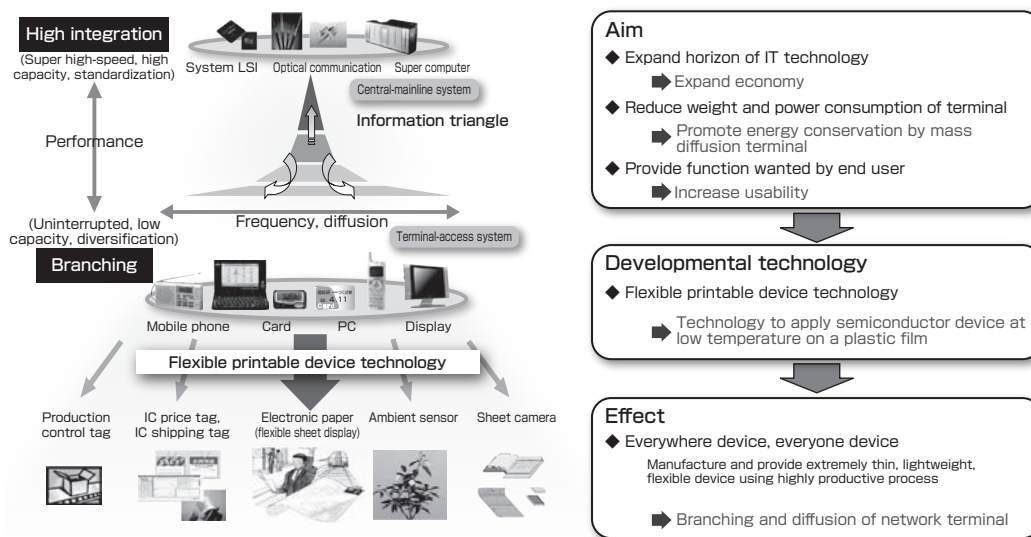


Fig. 1 Development of flexible printable electronics technology.

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their wish (everyone device). To respond to diverse individual demands, conventional technology that only fulfills uniform specification cannot accommodate individual demands, and is not economically feasible as industry. Therefore, it is necessary to develop technology that provides degree of freedom and can accommodate as much diverse specifications as possible.

On the other hand, with the recent rise in consciousness for energy conservation, there are demands for large-scale energy conservation in the semiconductor process (process innovation in semiconductor technology). Particular emphasis is break away from vacuum, high temperature, and photolithography processes. These are major social demands that cannot be ignored regardless of the target.

2 Objective of R&D

2.1 Toward prosumer electronics

To realize technology that may fulfill diverse demands of information terminal device such as “light and flexible,” “high productivity manufacturing,” and “wanted by consumer,” one of the major goals is to develop technology with high degree of freedom for accommodating diverse specifications, such as “flexible printable device processing technology” where the device can be fabricated on flexible substrate such as plastic and paper using solution process. At the same time, this technology enables low environmental impact process, and break away from vacuum and high-temperature processes. Therefore, this is an important technological goal that must be realized.

The ultimate goal of technology is to allow people to create what they want, that is, production of terminals by consumers themselves or prosumer electronics (prosumer = producer + consumer). If the ultimate goal is to have the information terminal device to reflect the user’s personality, then the technological goal will be to make the tools available at personal level.

To realize this goal, it is not sufficient to simply fabricate the device on flexible substrate with solution process, but the device must be fabricated with simple material and simple process (low-temperature application at 150 °C or lower) using simple machine. The Authors set these as technological goals and worked to meet this goal.

2.2 Match between needed function, device performance, and process condition

The information terminal device fabricated using these technologies must at least have performance required for intended use. Even if a technology has outstanding performance, it will not generate technological value if it is difficult to fit into the total system. On the other hand, even if a technology has inferior performance, it will be effective if it fits well in the system. The importance is the value

created when the technologies are fitted together in total. This is the concept of optimally consistent device. Therefore, in this R&D, the goals were to design device while clearly imaging the final product, to extract basic specification, and to develop technology that matches the process condition.

3 Development of key technology

3.1 Extraction of developmental technology

There are many elemental technologies that must be developed to achieve the above goal. We drew the scenario by extracting major technological issues and by presenting solutions, to show whether “flexible printable device processing technology,” which we used as symbolic concept, is realizable at all. For example, flexible device means fabrication of device using flexible material. The most suitable material to the flexible device is organic material, but when organic materials are used, there is always temperature limitation in processing. It is necessary to demonstrate that the device with required device performance can be manufactured at processing temperature 200 °C or less where the material will not disintegrate. Also, it is also necessary to show that using printing as processing method would secure processing accuracy to improve the device performance.

Therefore, we worked on technological developments to demonstrate that solutions were available for main issues, and obtained the following results.

3.2 Low-temperature application process

For lower temperature of manufacturing process, it should be a good idea to use alternative energy to heat energy for manufacturing. Since heat energy is transferred evenly and gradually over the reaction field, evenness is a major characteristic of film that is the other area where energy transfer is not required, as energy spreads gradually and evenly to all parts, and various sub-reactions take place. To avoid this, we developed a new technology to use alternative energy such as light and mechanical energies.

(1) Multiple-source photooxidation method

One of the important factors that may be the key to stable operation and high performance of device is SiO₂ insulating film. To form enough high-quality of a SiO₂ insulating film on the device, processing temperature of at least several hundred degrees is normally necessary. We developed low-temperature fabrication process, in hopes that the technological concept would be accepted if this important constituent of the device could be processed within the limit indicated in the specification (processing temperature 200 °C or less).

When a silicon compound reacts with oxygen at several hundred degrees, silicon dioxide (SiO₂) is formed. If this reaction can be occurred to form a high-density thin film by using soluble material, insulating layer of electronic device

can be obtained by liquid phase process. However, this is an oxidation reaction that normally requires high-temperature treatment at 500 °C or above after film preparation. It is known that catalysts is useful to reduce process temperature. However, this is not adequate for electronic device use because it often acts as impurities in the device. Therefore, we considered providing required energy locally using light energy, and tried to develop technology that would promote this reaction. As result, we succeeded in developing a new technique by introducing multiple-source photooxidation method (Figure 2)^[1]. Points for this new technological development were: selection of material with combined species that were less likely to be subject to stress failure on reaction precursor in forming SiO₂ film; selection of light source with sufficient energy to excite this combined species; and selection of separate light source sufficient to excite the active species to react with this precursor. Particularly, major point in appealing the significance of newly developed process is that the reaction can be promoted using a conventional light source such as lamp, rather than locally high-density energy source such as a laser. By keeping the maximum reaction temperature of the entire process to 200 °C or less, occurrence of defect due to contraction and expansion of film could be controlled, and as result, highly dense SiO₂ film was obtained. The formed SiO₂ film showed high resistivity over 10¹⁵ Ωcm and high dielectric strength over 7 MV/cm. This technology is currently considered for preparation of a dielectric layer of TFT for display use, especially for displays with flexibility and large size.

(2) Triaxial distributed pressure annealing method

Even for “flexible printable device processing technology,” there are major limitations in the specification depending on the technology used. For example, for electronic display of memo level information, the limitation of production cost is extremely severe. In this case, expensive material cannot be used. Low-temperature processing must be used and there is limit on usable materials, but it is necessary to show that technological application is possible under this condition.

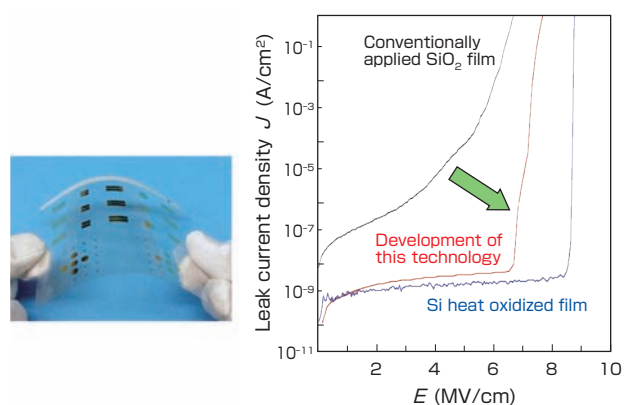


Fig. 2 Development of multi-source photooxidation method for forming dielectric layer by low-temperature printing.

Therefore, we developed technology to print wiring and electrode with low-resistivity on a conventional plastic film such as PET using conventional conductive inks. Conductive ink is normally thermally annealed at 400 °C or higher to reduce resistivity after forming the printed pattern. Recently, using nanoparticles of metals has been suggested to lower the annealing temperature. However if the material cost increases by using nanoparticles, the aforementioned objective is defeated. Therefore, we worked on low-temperature annealing technology to obtain low resistivity with conventional ink, and succeeded a new technique to reduce process temperature by using pressure as alternative energy to heat (Figure 3). Here, the point was also how to lower the temperature required for reaction. In this technology, low temperature was achieved by using pressure energy. Pressure energy was locally applied as anisotropic energy instead of applying energy homogeneously. That is, energy was concentrated onto necessary area and was not dispersed to surrounding area that did not require it. As result, in printing pattern using conventional silver conductive paste, we obtained resistivity 6×10^{-6} Ωcm at reaction temperature 120 °C or less (for comparison, resistivity of bulk silver = 1.6×10^{-6} Ωcm). Considering that heating to 200 °C or more was needed to obtain similar resistivity even when silver nanoparticle paste was used, it can be seen that pressure energy is extremely effective in lower temperature in annealing.

3.3 Printable device manufacture process

The greatest hurdle in developing printable device processing technology is whether the process specification requirement of being “printable” and the device specification requirement of being high performance can be both realized. For device performance, whether processing accuracy can be

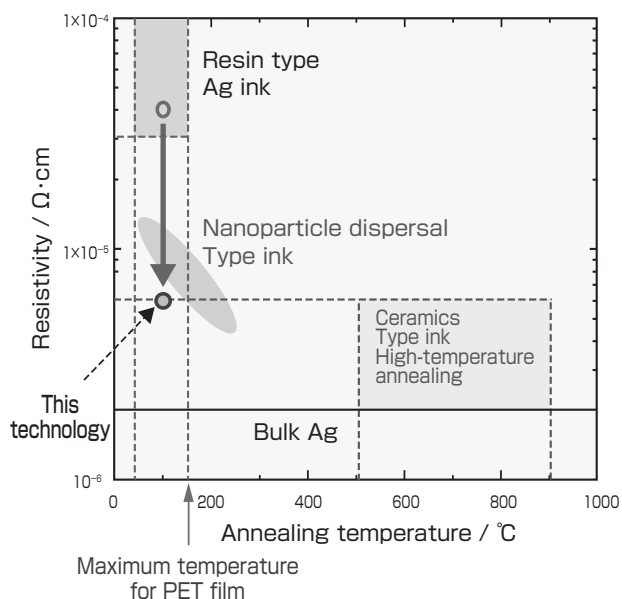


Fig. 3 Development of triaxial distributed pressure annealing method for forming low-temperature printed conductive pattern.

maintained is always questioned, since microfabrication control is required to some extent. Normally in liquid phase process, the microfabrication accuracy in in-plane direction is not high (up to several tens μm) when fabricating the device. Therefore, it was thought that transistor element that required high in-plane fabrication accuracy would not be able to perform sufficiently. Therefore, we decided solving this technical issue would be a breakthrough in establishing printable device manufacture technology, and started seeking solution.

Top & bottom contact transistor

As point of technological development, the fact that in-plane fabrication accuracy was only several tens of μm , must be accepted, and then we decided to employ elemental device structure design for constructing the moving part (channel) of several μm or less, which determined the device performance. Hence, we developed a new device structure named “top & bottom contact transistor” (Figure 4)^[2]. The channel size that determined the device performance required control of μm or less and was designed to be aligned in film thickness direction, so control could be provided by film thickness. By doing so, high fabrication precision in plane direction would become unnecessary. As result, it basically became possible to fabricate transistor with short channel by layers of printed lines, and we succeeded in forming channel length at sub- μm level. Using this element device structure, we demonstrated performance of 0.2V/dec or less for SS value, which is field-effect modulation factor of output current, for transistor formed entirely by printing using polymetric semiconductor with relatively high mobility ($\mu = 10^{-2} \text{ cm}^2/\text{Vs}$ level). It was shown that both manufacture process of being printable and high performance of device could be met simultaneously.

4 Scenario for industrial application

Explained above are the main elemental technologies that we developed. Looking at them individually, perhaps one can see technological value is very specific, singular technology. However, different world will emerge if one understands the scenario for development and positioning of the technology.

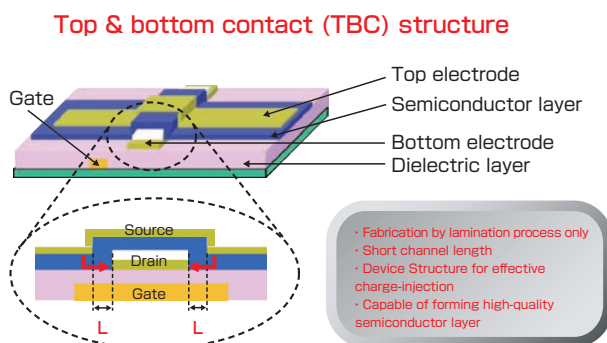


Fig. 4 Top & bottom contact (TBC) structure for forming all-printed element.

Next, the Authors will describe the scenario for technological development that was conducted toward industrial application.

4.1 Different demands from end users and technical users

Even if innovative technology is developed, unless we understand who wants such innovation, others may fail to see the appeal point of technology, and then it does not get introduced to the world. Therefore, we placed importance on analysis and understanding who wanted what. The demand of people who use it (end user) is the most important for information terminal device. Then, can technological demand be met by providing things that end users want? It is not that easy. Technological demand will not be valid unless it matches the demands of device producers or manufacturing companies. For example, say we can provide technology that enables production of highly usable terminal that end users will love at 10 yen apiece. However, even if one hundred million terminals are sold, sales is only one billion yen. Large corporations cannot do business, so they do not want this technology. However, it will be feasible for a small company. This is why we must ask, “Who will want this technology?”

4.2 Creating a player map

It is useful to create a player map to address the above question “Who will want this technology?” Since demands vary according to technological level even for similar technology, this map can be used to clarify the values of developed technology. Table 1 shows the technological phase, target product, and main target companies, and Table 2 is a player map that shows the technical issues in each technological phases and how they can be solved.

For example, there are many kinds of displays. It is necessary to combine several complex technologies for complex display such as for television (Phase I), and this is conducted by large display manufacturers. In this case, scenario of business development is determined by market demand, and the issue of pioneering technology development is whether to develop innovative technology that realizes the scenario or to provide technology that can respond to social needs.

Table 1. Development scenario.

Technological phase	Market example	Technological level	Technology user
Phase I	Television Mobile phone	Vacuum batch process	Major specialty company
Phase II	Electronic paper RF-ID tag	Roll to roll	Major emerging company
Phase III	Sensor Smart object	Conventional printing	Small & middle company
Phase IV	Label ID label Private manufacturing		Venture, individual

Next, new displays such as electronic paper (Phase II) do not require major technology as in television. Therefore, it is technology wanted by companies that wish to create new industry. In this case, new market must be pioneered, so discovery of function unseen in conventional technology will be the priority of development. However, there is limitation that the technology must be capable of fabricating relatively simple things. Although technology for simple display such as indicators and tags (Phases III, IV) may be simple, it can be technology from which totally new industrial product can be created, and it will be wanted by small & middle companies and ventures. Here, there may be more technological limitations such as unable to use expensive, special material or high cost manufacture technology, and therefore requires technological development dedicated for the purpose.

Some examples of what can be read from the player map are shown.

- ①Is the individual elemental technology to be developed in match with overall set-up concept? Are there any gaps in technology or player?
- ②Does the technology to be developed have chance of becoming leading technology?
- ③Is the technology to be developed something that can be developed in multiple directions?
- ④Can the technology to be developed gain competitive position?

The technological position can be seen clearly on the player map, and it is extremely useful in judging whether a technology will become winning technology. “Winning technology” is determined based on whether it can lead new industry (leading technology), can respond to social demands such as energy conservation (social technology), or whether it can support industries with weakness in technological development (small-middle company supporting technology).

4.3 Linear and non-linear models of technological development

Table 2. Player map of technological development.

	Material				Process	Device	Prototype
	Conductor	Semiconductor	Dielectric material	Peripheral material			
Phase I <small>For major specialty company</small>	Company	Company	Company	Company	Company	Company	Company
Phase II <small>For emerging company</small>	Company	Company	Company developed technology	Company		Company	Company
Phase III <small>For small & middle company</small>	Company developed technology		Company developed technology	Company developed technology			
Phase IV <small>For venture and individuals</small>	Company (developed technology)		Company (developed technology)	Company (developed technology)	University		
Basic		University	University		University	University	

There are two styles of technological development: linear model where clear, integrated goal is set and development is planned toward achieving that goal; and non-linear model where clear, integrated goal is difficult to set although target image is sort of there, and scenario to get to the goal is unclear, and appearance of jump-up technology is awaited (Figure 5). The latter non-linear model of technological development is often employed when specifications are diverse as in information terminal device technology.

In the non-linear model of technological development, there is expectation for jump-up technology, and it is difficult to conduct development in an orderly manner. However, analyzing the technological fields that employ this model, there are many exceptions. The “information terminal device technology,” the topic of discussion in this paper, is one example. There is gap in technology because there is no technological player, and it looks as though people are waiting for jump-up technology to fill in the gap. In this case, clear planning can be done by organizing the existing technologies.

4.4 Presenting effectiveness and innovativeness of technology as product

It is effective to present the developed technology, even if it is single technology, as prototype by combining it with related technologies. The point is to show that technological development can be done by using set of technologies, and to take lead in the technological concept. However, important point is to deliver clear message as well as fabricating a prototype and showing its function. For example, in the above development by the Authors, we added unique message. For “multiple-source photooxidation method,” our goal was to use it in printed TFT for display. In the initial stage of prototype fabrication, we were first in the world to succeed in showing moving image in color on organic TFT driven LC display (Figure 6)^{[3]-[5]}. As this was time when many have high expectation for printed TFT technology, our demonstration

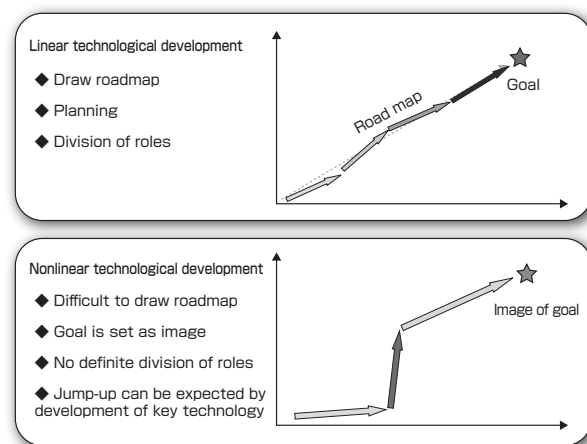


Fig. 5 Linear model and nonlinear model of technological development.

became news throughout the world. In this technology, we communicated the message that in the future this technology will enable large-surface, ultra-thin, wall-type screen television, and appealed high reliability and ability to fabricate large surface area in addition to high performance.

“Triaxial distributed pressure annealing method” was demonstrated by creating prototype all-printed RF-ID tag (Figure 7)^[6]. It was shown that RF-ID tag could be formed on a film by printing only for the first time in the world. It contained message that in near future, flexible information terminal would become available, and we were able to appeal our goal of technological development.

The above examples of technological developments are not fabrication methods of active layer (semiconductor layer) that generally draws more attention, but are formation technology of electrodes, wiring, and dielectric layer that are often left behind. There is another reason for presenting our development effort in these left-behind technologies, and that is to fill in the player gap. In certain technological concept, attractive elemental technology attracts many players of technological development, and certain degree of technological advance can be expected. However, in aforementioned elemental technologies, development does not take place, not due to technological hurdle, but due to other factors such as business. In this case, it is difficult to find set of technologies even if one wanted to. In some cases, technological concept cannot be “totally consistent.” Therefore, to appeal that the technological concept can be totally consistent, it is necessary to attempt filling the gap in

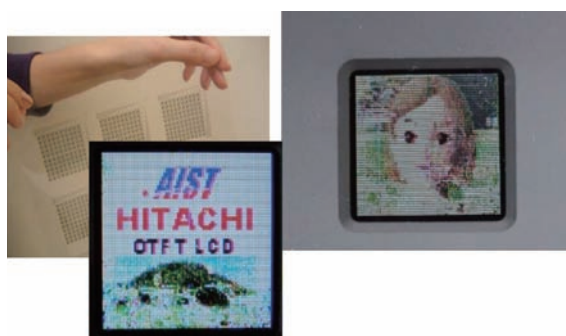


Fig. 6 Development of organic TFT driven color LC display.

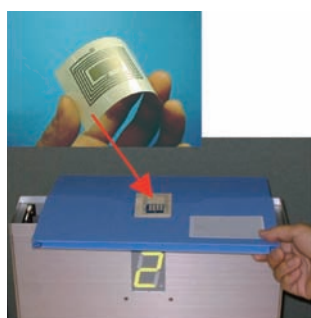


Fig. 7 Development of all-printed flexible RF-ID tag.

technology. It is concept of technology for that “last piece” to completion. As researchers at national institution, we decided to play the role of showing that development concept can be provided in total set, to show leadership for the direction of technological development, and to reduce risk of development efforts by the industry.

We shall give specific example of practical application of this effort. As side-development of printable device technology (top & bottom contact transistor technology), we developed 3-dimensional nanoporous device (Figure 8)^[7]. This is device technology designed to effectively utilize wall fabrication that is one of the characteristics of liquid phase process, and we created a device (agricultural sensor) that enables highly sensitive measurement of substance that passes through or are incorporated into the pore of the porous material. This was technology developed as result of request from end users (farmers). The request was to develop highly sensitive agricultural sensor that can be used easily by farmers, for product control of produce. Considering the set of technologies, materials were available, fabrication process could be done readily with current technology, system developers existed, and of course, there were users. Only factor nonexistent was device developer. Here, there was “gap in technological.” In this case, there were no technicians who would work on this technology since it was not profitable. Therefore, as researchers of public institution, we decided to engage in “division of role for risk sharing” where we would actively take up elemental technology with high risk of development. As result, we created terminal device that was provided through set of technologies (Figure 9)^[6]. This was effective in delivering strong message for prosumer electronics. Forms and specifications of the attached sensor had to be changed according to the type of produce. Also, places where sensors could be attached were different. Moreover, the sensor must not interfere with the produce. We launched this product with message that the information terminal device that can meet various and specific needs can be developed jointly with actual user (agricultural experiment station).

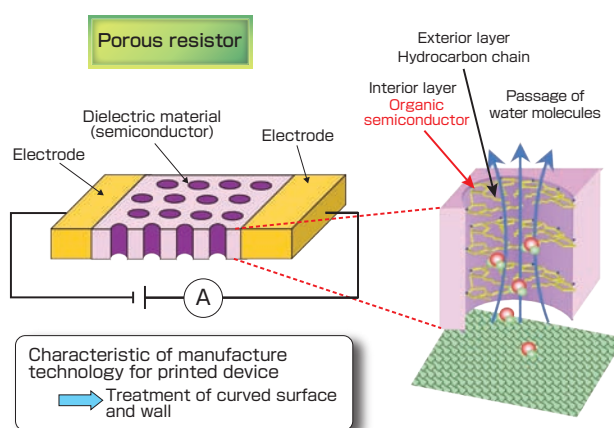


Fig. 8 Development of 3-dimensional nanoporous device for flexible sensor.

We believe that the greatest significance of our prototype was to show the validity of technology, that sufficient performance could be obtained when technologies are used in set. We were able to appeal the attractive point of technology that we could create things that we never saw before (Figure 10).

It is uncertain whether the prototype itself will be taken up by companies for final product realization. However, we think delivering messages will contribute greatly to corporate decisions of whether to employ these technologies as targets of realization.

5 Future issues and developments

As described above, the field of information terminal technology to which printable device processing technology is being applied has characteristic of becoming more branched as it diffuses further into the society and the required technological specification becomes diverse. If one jumps into development to meet each and every demand, there will be as many technologies as demands, and strategic, planned technological development becomes impossible. As effort to be strategic, we placed particular emphasis on planar and continuous aspects of future technological development.

5.1 Set of technologies and timing

For industrial technology today, it is extremely difficult to achieve technological concept with single technology. In many cases, technologies from different fields are required to supplement development. In case the target is current and the developed technology is intended to replace current technology, it is probably not necessary to pay attention to related technologies. However, in case the goal is new technology that may lead to creation of new market, that is, if it is pioneering technology, it is mandatory to pay attention to combination with other technologies, and build a technological system. Therefore, planar development or development of set of technologies is important.

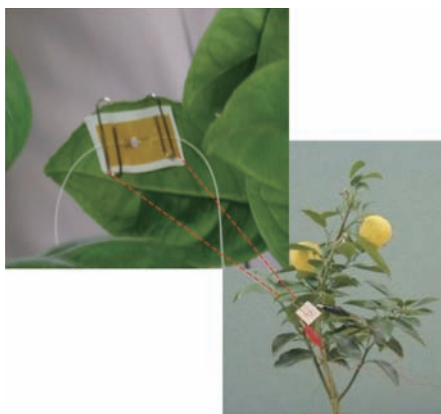


Fig. 9 Development of flexible transpiration sensor for agricultural use.

There is one important point that must not be forgotten. That is the concept of development phase or knowing where the currently developed technology is positioned. Grouping technologies into set is routine, and companies that engage in development as business do so regularly. However, when time concept of development phase is considered, one realizes that it is not a singular concept. The company starts grouping technologies into set only when the technology is near completion and enters the phase when the overall scenario becomes visible. Even a company must struggle with a single technology for which the scenario is unclear, and must wait a while before the scenario can be written.

Another point is that to aim at target that couldn't group technologies into set because there was "gap in technology." This means that the technologies could be bundled together only after development of new technology. Since this often leads to new products and new industry, it is worth working hard. In corporate activity, when gap occurs in area outside the company's technological domain, nothing can be done and the development may have to be given up.

Therefore, the issue is who will be the first to present the scenario for industrial development. For industrial technology, the key point is to discern which is technology that is likely to win, and that is what we pursued.

5.2 Continuous development leads to early diffusion

Moreover, continuous development of technology, or pioneering of next technology, is very important. How technology is developed as industrial technology under which scenario is extremely important for realization. It is particularly important in our field where technological development tends to be single shot. Single-shot technology may be useful to meet special demand but its wide diffusion may be difficult. On the other hand, showing the second and third hands for technology that others find interesting presents the depths of the technology and is useful in drawing more attention. As result, speed of diffusion into the industry will increase for related technologies. That is why it is important to continue pioneering technology and to present scenario of how the technology will grow.

Scenario for goal realization

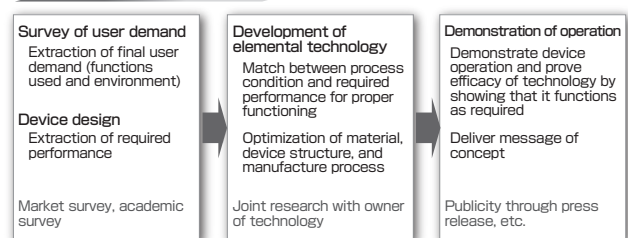


Fig. 10 Scenario for realization of flexible printable electronics.

6 Conclusion

We were able to engage in research and produce results acceptable to the society, because we formed research teams where the members worked closely and each R&D could mutually supplement each other. In this point, there is definite advantage of organized research. On the other hand, steady academic activities are at the basis of multi-faceted technological development. Without work in *Type 1 Basic Research* and academic societies, there might have been less interest in our technology.

In the future, we plan to work as team on the technological development to create new industry, while balancing *Type 1* and *Type 2 Basic Researches* and by presenting scenario for development of industrial science.

Note

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Discussion with Reviewers

1 Positioning of flexible-printable device processing technology

Comment (Hiroshi Tateishi)

If my understanding that the research objective of this paper is expressed by its title “development of flexible-printable device processing technology” is correct, I think the description of social value of this research objective is insufficient. Specifically, there is a gap between specification required for information terminal device - various uses, everywhere device, everyone device - and the concept of flexible-printable device. Flexible-printable device is one of the options that fulfill the above specification, and I don't think it is everything. Unless you provide details (or specifications) about the condition in which flexible-printable device becomes best choice among several candidates, the argument will be flexible-printable device first. Demand for energy conservation during manufacture process is not sufficient as explanation. I think the explanation on why this device is necessary or effective for certain demand is lacking. This problem is apparent in Figure 1. There is a clear gap between the layer surrounded by “branching” and flexible-printable device. According to this figure, it seems that the flexible-printable device will solve all problems, but I don't think things are so simple.

Answer (Toshihide Kamata)

Information terminal device technology has been called as ‘low-end target’, and many people hold impression that it is accessory technology that can be accomplished when high technologies are employed. Contrary to such perception, this technological field is not really pioneered, and placed in situation where there is almost no technology applicable to industry use. This is because there is no matchmaking between technological demand and market demand, and it shows that industrial technology cannot be developed from technological indicator alone. If I accept your point, I think we will fall back into this vicious cycle where things are built up from technological indicator. To break this cycle and to pioneer technological field, one good method is to present an example of symbolic technology that may solve this issue and pull the technology under its flag. In this paper, the concept “development of flexible-printable device processing technology,” which we perceive as the best technological indicator right now, is used symbolically to explain the technological strategy for pioneering this technological field. The social value of this strategy is to lead the expansion of information terminal device technology, which is stalled at this moment. Therefore, to discuss the details of other supplementary technologies will divert the main point under discussion, and I think describing them in this paper will bring about an adverse effect.

Comment (Naoto Kobayashi)

What are the main competing technologies in the R&D for “flexible-printable device processing technology”? For example, I think there are cases in which one uses not only organic devices but also heterogeneous materials and devices such as inorganic semiconductor and glass materials and other cases in which one uses different synthetic method and process with the same organic devices. I think it will be easier to understand if you show comparison of performances (benchmark) targeting for a certain purpose. You wouldn't have to show all examples, but I think you should show some characteristic examples.

Answer (Toshihide Kamata)

I've added some remarks in the text. In technological development there is linear model where goal is set and research progresses according to plan, and nonlinear model where goal setting and planning are difficult although there is a final image, and here, I am engaging in discussion on how to conduct technological development by nonlinear model.

Although people often think that the nonlinear model advances by flash insight, I am trying to show that it is possible to conduct logical and planned technological development by employing method where overall map is drawn (overall systematization) and some important points are extracted. Therefore, I believe the nonlinear method for creating research plan is, rather than starting from material science such as organic or inorganic materials, to consider materials systematically from physical property axis of flexibility, chemical property axis of solubility and so on. The optimal materials are then selected according to situation one after another.

The important point is not to create a monoaxial technological development plan by setting benchmark for one technological indicator, but to plan by creating a map and discerning technological matches (several may be present), and to sharpen those areas. I want to express that this method is appropriate in this technological field. For this reason, I think the range of technological development will be narrowed if thing starts from technological seeds.

Comment (Hiroshi Tateishi)

I looked at Figure 1 again after reading your response, and perhaps this figure is the starting point of why I was misled. Since there is picture of flexible-printable device technology beneath ‘the central-mainline system → terminal-access system’, I perceived unconsciously that “flexible-printable device technology will replace current terminal device technology.” Perhaps although they exist at the same level in that they are “terminal devices,” we should understand rather “flexible-printable device technology is a development in different direction.” While current technology is, in general, characterized by the fact that they are “general-purpose technology that can do anything,” flexible-printable device technology should be understood as “technology of simplified function that specializes in particular demand of end user.” However, if necessary technology is different for each device, it will not be economically feasible, the manufacturing technology for flexible-printable device must be “general and has degree of freedom that allows accommodation of various demands” or else it will not help expansion of this technology. I think this will be the main point of the paper. If my understandings are correct, can you please add this point in the paper?

Answer (Toshihide Kamata)

Thank you very much for spelling out the main point of the paper. The above comment is indeed what I wish to emphasize. I made some additions to the introduction.

2 Direction of technological development

Comment (Hiroshi Tateishi)

I feel that the expression “phase” used in Tables 1 and 2 is strange. Normally, phase implies that it is developed one after another, but the phases here do not seem to evolve in order IV → III → II → I. Isn't it closer to “level”?

Answer (Toshihide Kamata)

The “technological phase” described here develops in order I → II → III → IV, and I feel the word ‘phase’ is appropriate. Your indication “evolve in order IV → III → II → I” is incorrect understanding, and it is extremely important to understand to read this paper. It is not necessarily true that more complex technology will be developed as technology approaches the end user, such as information terminal device. That is because there will be no development as industrial technology unless there is match between the demands of user and manufacturer. For example, Phase I is technology where the intent of the manufacturer is easily reflected since it is strongly characterized as mass production of uniform standard. Because technology provider

and producer both exist, marketing as industrial technology is done relatively quickly. However, Phase IV is technology for users. Since manufacturer may not see business opportunities, it is less likely to be taken up by producer and technology provider, and therefore it is not likely to be pursued as industrial technology. Therefore, the technology corresponding to Phase IV lags behind compared to Phase I in terms of indicator of degree of success in industry, rather than indicator of technical ease/difficulty. It can be said that technology develops in branches in order of Phases I → II → III → IV.

In this paper, one of the main arguments is to raise issue on how to develop technology that is difficult to market from the technology oriented strategy, yet in demand by many people (users).

3 Role of AIST

Comment (Naoto Kobayashi)

The development scenario of Table 1 and player map of technological development of Table 2 are extremely useful and unique attempt to describe this field. If the technology aims to become “prosumer technology” in the future, a place (time and space) for the developer, the technological user, and the end user to closely exchange opinions will be important. Do you have any good ideas for such exchanges?

Answer (Toshihide Kamata)

Prosumer technology, in other words, is a concept of “self sufficiency,” and ultimate venture when seen from another angle. Therefore, I think we must do away with the concept of role sharing, because I feel that if people are asked to exchange opinion based on their assigned role, things are less likely to be realized. For actual realization, I think it is important to raise consciousness: “I will be the implementer of prosumer technology.” To accomplish this, it is necessary (1) to set up place for providing technological information, (2) to present model for taking leadership in methodology, and (3) to provide tool for actual implementation. Among these, I think, (1) and (3) should be positioned as public service from perspective of risk sharing. For (2), it is like showing a new technological lifestyle such as a second job. Public institution like AIST should suggest and show example of style of industrial technological society for both cases.

Question (Hiroshi Tateishi)

Looking at Tables 1 and 2 from the viewpoint of Discussion 1, I understand that the concepts are organized well, but there is no description of the positioning of AIST (Kamata Group). Is it possible to specifically describe the AIST strategy in these tables?

Answer (Toshihide Kamata)

Since this is a published paper, I avoided being too self-assertive, and I consciously refrained from the “we are” tone. Yet in fact, the analytical statement of this paper strongly states the position of AIST and our aim (leadership in technological concept, risk sharing, etc.). As you indicate, I consciously added the subject “we” in the revision.

4 Basic concept about technological development

Question (Naoto Kobayashi)

To consider material, process, and element as a set of technologies is extremely important. I also think the concepts of continuous development and planar development, where the integration with heterogeneous technologies that must be used for supplementation, are also important. I think these are common to the development of industrial technology in general. Are there any other characteristic issues unique to R&D for “flexible-printable device manufacture technology”?

Answer (Toshihide Kamata)

In technology in which many of the specs are determined by the end user, such as in information terminal device technology that “flexible-printable device manufacture technology” is involved, technology tends to be used for small-volume multiple-products, and the technological development takes nonlinear model without uniform indicator. In this case, if just one of the technological concepts does not fit with manufacturer’s business concept, it does happen that consistency in material, element, and module cannot be maintained. As a result, in many cases, the technological concept fails to bloom as

industry. There appears “a gap of technology” in a series of elemental technologies, and technological blossoming fails due to this limitation. Moreover, this “gap of technology” occurs not because of technological difficulty but due to business concerns, and no player is likely to show up no matter how long one waits.

The concept of “planar development” described in the paper does not express the necessity for grasping the overall picture to check our position, rather it tries to express the necessity for grasping the overall picture to prevent “gap of technology” as well as the fact that there are issues that must be tackled by players who share the risk in areas of “gap of technology.” Also, I emphasized “continuous development” because I wanted to solve the problem that “technological development seem to be for single target application and one cannot see the depth of technology,” which is common issue for technology for small-volume multiple-product application. By providing specific case where technology that may seem like single technology application can be developed sideways, we wanted to show the depth of technology, and that it is necessary to lower the entry barrier as player of technological development.

Question (Naoto Kobayashi)

I understood that the synthetic method as *Type 2 Basic Research* for this work is described in details in 4.4 “Presenting effectiveness and innovativeness of technology as product.” Particularly, you explain that “multiple-source oxidation method” and “triaxial distributed pressure annealing method” are “supporting role technologies” that fill the “gap of technology,” but the whole technology will not be complete without them, so I think they are extremely essential. As a synthetic method, it is understood as ‘built-in type’, *i.e.*, putting in the last piece to complete the whole puzzle. If this is the case, you may need an expression that emphasizes such role (rather than supporting role). What do you think about this, including my interpretation?

Answer (Toshihide Kamata)

I realize that “supporting role technology” is somewhat negative expression and not appropriate. As you indicated, it is technology absolutely necessary for total design. I changed the expression to “gap-supplementing technology” → “gap-filling technology” and “supporting role technology” → “last piece technology”.

5 Strategy to assess individual elemental technology

Question (Naoto Kobayashi)

You have indicated that, “a device may not be created even with extremely superior technology, but even if some parts are inferior in performance, it may become effective technology if there is a good total performance.” This seems very important. If this is called an ‘*optimally consistent device*’, it depends on technological development strategy that how many individual elemental technologies composing the device are allowed, and that how much higher performance is sought in some of the composing technologies. Do you have any idea on how to assess them (or to determine what the optimum is)?

Answer (Toshihide Kamata)

Considering the fact that technology is accepted as it has advances against the existing ones, I think “optimal consistency” must be understood as function of time. Technology will be accepted if people can see clear differentiation against current status. However, it will not be accepted if the step of advancement is too big. Therefore, I think the first point in assessing technology is to recognize that “optimal consistency” must always walk in time, and to make sure that the differentiation can be clearly discernable in the footstep. How assessing is done means being able to recognize the differentiating point. I think it is important for the developers to go out in the society and brush up the feeling when they become a regular member of the society. I want to repeat the point again that in our technological field, technological specification is determined overwhelmingly by end user rather than manufacturer, and the important point is how to be socially oriented rather than technologically oriented.

A new density standard replaced from water

— Using silicon single-crystals as the top of traceability in density measurement —

Kenichi Fujii

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Water is conventionally and widely used as a reference standard to measure physical quantities such as the density, volume, internal volume, and concentration. Water is also used as a standard for other physical properties such as the specific heat and surface tension. However, water density is influenced depending on its isotopic composition and content of dissolved gases. Researches on density measurement using solid material with stable density such as silicon single-crystals were therefore started in the 1970s. Demands have been raised from industry for densimetric technology to improve reliability of product and to maintain traceability of measurement. With this background, AIST established a new density standard using silicon single-crystals. Shifting the density standard from liquid to solid will not only improve the accuracy but also promotes development of new material evaluation technology for thin films as well as metrological standard technology for next generation.

Keywords : Density, standard, water, silicon single-crystals, traceability, Avogadro's constant

1 Introduction

Water has been used as a density standard since ancient time. The International Prototype of the Kilogram (IPK) currently used as the standard of mass was originally defined as the mass of one liter of water measured using the Prototype Meter created at the end of the 18th century^[1]. In the International System of Units (SI, from Le Système International d'Unités)^[2], the unit of density (kg/m^3) is the SI derived units composed from the SI base units, kilogram (kg) and meter (m). To measure the density according to the definition of SI, only mass and length standards are needed, and it seems there is no necessity to establish a new standard for density. However, to start from absolute measurements of mass and length to measure the physical quantity of density, large-scale measurement facility is required and measurements are extremely difficult, and it is much easier to make a relative density measurement of unknown material with respect to the density of material whose absolute value is already known accurately. Therefore, general method used is to measure the absolute value of density of a widely available material with high reproducibility, and then to make relative measurement of unknown material using this substance as a reference standard. The material that serves as the standard for density is called density reference material or density standard material^{[3][4]}.

Water is a density standard material that was used first, and has been used widely to calculate the density and volume of other materials. The absolute measurement of the density of water was done by the Bureau International des Poids et Mesures (BIPM) around 1890 to 1910^[5]. Since this measurement was conducted before the discovery of isotopes, the issue of uncertainty caused by the ambiguity of isotopic composition of water remained. Therefore,

several international organizations such as the International Union of Pure and Applied Chemistry (IUPAC) issued a recommendation to re-measure the absolute value of the density of water with known isotopic compositions at the relative combined standard uncertainty less than 1×10^{-6} in density. In response, the Australian Commonwealth Scientific and Industrial Research Organisation (CSIRO)^[6] and the National Metrology Institute of Japan (NMIJ, formerly the National Research Laboratory of Metrology)^[7] conducted independent absolute measurements of the density of chemically pure water with isotopic composition equivalent to the standard mean ocean water (SMOW)^[8] in 1990s. The independent absolute measurements were thus obtained by Australia and Japan. Since there was a relative density difference of 2.1×10^{-6} that is greater than the uncertainty between the two values, the two data were analyzed by the Working Group on Density (WGD) of Comité Consultatif pour la Masse et les Grandeurs Apparentées (CCM), Comité International des Poids et Mesures (CIPM), and recommended values for the density of water having isotopic compositions equal to SMOW have been issued in a range 0 to 40 °C with the absolute value of $999.9749(8) \text{ kg/m}^3$ at 4 °C and 101.325 kPa^[9]. The number in parenthesis expresses the expanded uncertainty ($k=2$) of the last digit. This value is widely used as the internationally recommended value. However, the density of water changes due to effects of dissolved gases and isotopic compositions, and several corrections are necessary depending on the actual condition of the water sample.

Other than water, mercury has been used as a standard for high density. Absolute measurement for the density of mercury was conducted by the National Physical Laboratory (NPL) of UK in 1957 and 1961 to establish the standard for pressure^{[10][11]}. When the average values of

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these measurements are converted to ITS-90, the current temperature scale, the density at 20.000 °C and 101.325 kPa is $13\,545.854(3)$ kg/m³ [12]. Although the relative combined standard uncertainty of the measurement is reported to be 0.2×10^{-6} , due to differences in isotropic compositions, there are relative deviations of about 1.7×10^{-6} in the density of mercury samples from different places of origin. Therefore, the relative combined standard uncertainty of the density of non-calibrated mercury is thought to be larger than 1×10^{-6} [13]. The uncertainty of the density of mercury not only affects the pressure standard [14], but also remains as the major uncertainty source in the absolute measurement of the universal gas constant R determined by the spherical resonator [15] and absolute measurement of Josephson constant $K_J = 2e/h$ (here, e is the elementary charge and h the Planck constant) determined by the mercury electrometer [16].

Since conventionally used liquid density standards have problems caused by inconsistencies in the measurements and uncertainty in the isotropic compositions, it is extremely difficult to construct a density standard with a relative uncertainty smaller than 1×10^{-6} from these data. On the other hand, the demands to accelerate the global Mutual Recognition Arrangement (MRA) and to clarify traceability of measurement have increased in the field of measurement standard. Particularly, there is increasing necessity for measuring the density in a way traceable to the definition of SI. In industry, density sensors with high-sensitivity such as vibrating tube densimeters are already used widely, but it has become difficult to provide sufficiently accurate density standard from conventional testing and certification for hydrometer calibration conducted under Measurement Law. Particularly in the brewing industry, alcohol concentration of alcoholic beverages are determined by density measurement using the alcohol table, and introduction of vibrating tube densimeters allowing automatic and high precision measurement had been considered. Therefore, there was increasing demand for building a traceability system in the Japan Calibration Service System (JCSS) established in the Measurement Law.

Recently, high precision density standard has been required from science and technology such as the redefinition of SI and the determination of fundamental physical constants. Particularly, experimental research to redefine the kilogram, which is the only SI base unit still defined by material artifact, is being conducted by NMIJ and other national metrology institutes [17]. In the x-ray crystal density (XRCD) method to determine the Avogadro constant from absolute measurements of the density, lattice constant, and molar mass of silicon single-crystals, an absolute measurement of the density of isotopically enriched silicon single-crystals at a relative standard uncertainty of 1×10^{-8} is required [18].

Considering these circumstances, AIST decided in 2001 to

build a new density standard with silicon single-crystals as the top of traceability, and started providing reference standards for solid density that could not be handled by conventional measurement methods. To date, we have provided a new density standard traceable to the definition of SI to industries and users by developing new calibration technologies for hydrometer, density standard liquid, vibrating tube densimeter, solid material, thin film, and PVT properties.

2 Need for new density standard

2.1 Social demand

In petroleum, alcohol, brewing, and food industries, density of liquids is measured during manufacturing process and for quality control. Particularly, accurate measurement of alcohol concentration is essential for quality control of alcoholic beverages, ingredient labeling, distribution, and fair assessment of alcohol tax. In the Measurement Law, Specific Measuring Instruments are set for important measurements in certain economic activities and services, and Type Approval is conducted for the structure and specification of the measuring instruments. For the density measurement of liquids, standards are provided for density, specific gravity, and alcohol hydrometers. Hydrometer, also called the “float,” is a measuring instrument for density, and the scale of the alcohol hydrometer is calibrated using the alcohol table [19] that shows the relationship between the alcohol concentration and the density. Hydrometer scale was conventionally calibrated using the density of water. However, due to its structure, it is easily influenced by the surface tension of the liquid sample, so the relative standard uncertainty of density measurement by hydrometer is limited to be about 0.01 %. The relative standard uncertainty of alcohol concentration measurement based on this measurement is therefore about 0.1 %. Although this method is inexpensive, its scale must be read visually by the operator, and cannot be readily automated.

The measurement method most widely used by the National Tax Agency (NTA) for assessing alcohol tax was the alcohol concentration measurement using alcohol hydrometers. Alcohol hydrometers certified according to the Measurement Law must be used in the Official Analysis Method of the NTA. This is because the data used for tax assessment must be fair, and the alcohol hydrometers certified by the Measurement Law was the only available alcohol measuring instrument with third-party verification.

On the other hand, the demand for more precise density measuring instrument had increased in the brewing industry to improve quality control and to introduce automation. The industrial demand was to measure alcohol concentration at an uncertainty of 0.05 % for fine control of manufacturing process, and it was therefore necessary to supply a new density standard traceable to the national standard with an uncertainty of 0.005 %.

Vibrating tube densimeter is a density measuring instrument with extremely high resolution, and the most stable instrument can measure the liquid density with a reproducibility of 10^{-6} to 10^{-7} . Although vibrating tube densimeters had already been introduced experimentally in the brewing industry when the issue was first investigated, it was necessary to calibrate the relationship between the density and vibration frequency using density standard liquids. It was necessary to supply such density standard liquids with third-party certification at a relative standard uncertainty of about 0.001 %, but there was no system for providing traceable density standard liquids in Japan.

2.2 Scientific needs

Speed of light in vacuum c , the Planck constant h , elementary charge e , and the Avogadro constant N_A are fundamental physical constants that are used to describe nature. If such fundamental physical constants are determined in conformity with the definition of SI, various fundamental physical constants can be derived from them. Because the values of fundamental physical constants are of primary importance for science and technology, the Task Group on Fundamental Constants that was established in the Committee on Data for Science and Technology (CODATA) of the International Council for Science (ICSU) summarized the recommended values of fundamental physical constants through a process of adjustment so that rigorous relationships among them are kept in a consistent way^[20].

The Avogadro constant is important not only for adjustment of the fundamental physical constants, but also to define the unit mole (mol) for the amount of substance. Moreover, if the Avogadro constant can be determined with a sufficiently small uncertainty, it will become possible to redefine the kilogram, the only SI basic unit still defined by material artifact, based on mass of an atom or fundamental physical constants^{[21][22]}. Therefore, Conférence Générale des Poids et Mesures (CGPM) that was organized under Convention of Meter recommended experimental studies to redefine several SI basic units including kilogram using fundamental physical constants and to evaluate the mass stability of the International Prototype of the Kilogram (IPK) under cooperation of national metrology institutes throughout the world.

Technology to measure the density of silicon single-crystals with a small uncertainty plays an important role in the determination of the Avogadro constant by the x-ray crystal density (XRCD) method. In the XRCD method, the Avogadro constant N_A is derived by $N_A = 8M/(\rho a^3)$ from absolute measurements of the density ρ , molar mass M , and lattice constant a of silicon single-crystals. In 2005, the NMIJ, the Physikalisch-Technische Bundesanstalt (PTB) of Germany, and the Institute of Reference Materials and Measurement (IRMM) of the Europe Joint Research Center collaborated to measure the Avogadro constant from silicon single-crystals

with natural isotropic compositions, and achieved a relative standard uncertainty of 3×10^{-7} , which is the highest accuracy achieved by the XRCD method^[23]. In 2007, the International Avogadro Coordination (IAC) Committee organized by the CIPM, under cooperation of eight research institutes around the world including NMIJ, prepared a single-crystal from highly enriched silicon isotope ^{28}Si for improving the uncertainty of the Avogadro constant to 2×10^{-8} , and the research continues toward the redefinition of the kilogram. To achieve this goal, it is necessary to determine the density of silicon single-crystals with a relative standard uncertainty of 1×10^{-8} .

The Avogadro constant determined from silicon single-crystals is also used to verify theories in the AC Josephson and quantum Hall effects^[20]. The electric potential difference generated by the AC Josephson effect is expressed as $U = nf/K_j$ (n is integer, f is frequency of microwave irradiated onto the Josephson junction device, $K_j = 2e/h$ is the Josephson constant), and the electrical resistance realized by the quantum Hall effect is expressed as $R = R_K/i$ (i is integer, $R_K = h/e^2$ is the von Klitzing constant), and these are important fundamental theories in establishing the electrical standards. However, since whether the electric potential difference and the electrical resistance are exactly quantized by $2e/h$ or h/e^2 cannot be proven by theories, work to verify the theory in the range of uncertainty of experiment is conducted by comparing and investigating with values such as h and e obtained from experiments that do not depend on the AC Josephson and quantum Hall effects. In the Task Group on Fundamental Constants of CODATA, the value for the Avogadro constant obtained by the XRCD method is used as an input quantity because the value for h is obtained from the Avogadro constant without relying on the AC Josephson or quantum Hall effects. From these investigations, it is now verified that the AC Josephson and quantum Hall effects are correct with an uncertainty of about 10^{-7} ^[20].

2.3 Scenario for achieving the goal

It is necessary to clarify the R&D policy to achieve the goal by satisfying both the demands from society and science. The policies are summarized as follows:

- (1) To set the National Primary Standard (the highest order standard in Japan) for density that is traceable to the definition of the SI basic units.
- (2) The primary standard of density must have function that can meet the demands from society as well as future needs in science.
- (3) To be able to calibrate the users' measuring instrument such as hydrometer, density standard liquid, and vibrating tube densimeter by unbroken chain linked to the primary standard of density.
- (4) To create a system where the density calibration service can be provided by registered calibration service

provider certified according to ISO/IEC17025 standard used in the Japan Calibration Service System (JCSS).

(5) To ensure that the highest order standard of registered calibration service is sufficiently stable, and does not require frequent calibration by the primary standard owned by the AIST.

When working on (1) of the above policies, we considered designating water as the standard of density by determining the purification method, purity analysis, and isotropic composition measurement of water. However, despite maximum technological effort, it is still extremely difficult to have a relative uncertainty of better than 1×10^{-6} . On the other hand, densimetric technology for silicon single-crystals, which was developed at the AIST for determination of the Avogadro constant, had already reached the level of 1×10^{-7} . Therefore, we selected the density standard system with silicon single-crystals as the top of traceability. Item (5) was an important factor when considering the necessary work at the registered calibration service providers. We discussed this point with candidates of service providers, and reached conclusion that even if the initial investment for calibration facilities was somewhat high, in middle to long-term, it would be easier for the service providers to have their own stable density standard for maintaining reliable calibration, as they would be freed from frequent calibrations of their own density standard. Based on these considerations, AIST started working on the new density standard system.

3 Development of new density standard system

Since density of silicon single-crystals is extremely stable, the National Institute of Standards and Technology (NIST) of the USA considered using it as a solid density standard for first time in the 1970s^[24]. When the CSIRO developed the technology of polishing a 1 kg sphere from silicon single-crystals in 1987^[25], it became possible to directly determine the density from mass and dimensional measurements, and thus it opened a new way for substantially reducing the uncertainty of density measurement. Conventionally, the density of silicon single-crystals had been calculated from buoyancy force measurement in a liquid^[24], using the volume standard realized by steel spheres whose volumes had been determined from dimensional measurements. By polishing silicon single-crystals into spherical form, the absolute value of the density could be obtained directly without buoyancy force measurement. In order to use the silicon sphere for determination of the Avogadro constant and not just for a density standard, CSIRO developed a new manufacturing process using mechano-chemical polishing as well as mechanical polishing at the final phase, to prevent crystal damage near subsurface^[26]. In cross-sectional observation near the sphere surface by transmission electron microscope, it was verified that crystal structure was maintained until it transformed to surface oxide layers. Using this polishing

technology, it is now possible to obtain a sphere with a diameter about 94 mm, mass about 1 kg, sphericity (maximum deviation from mean diameter) 50 nm, and surface roughness 0.1 nm. AIST noticed the excellent characteristic of the silicon solid density standard when the polishing technology was first developed at the CSIRO, and started working on a new density standard system that will replace water^{[27]-[30]}.

3.1 Characteristic of silicon solid density standard

Silicon is a fundamental material in the semiconductor industry, and highly pure, dislocation-free, large size single-crystals are obtained readily. Since there are three isotopes ²⁸Si, ²⁹Si and ³⁰Si, the density of individual silicon crystal may relatively vary about 1×10^{-5} due to variations in natural isotropic compositions and mass fractionation effect during the crystal growth, but their mean density value is about 2329 kg/m³ at 20.000 °C and 101.325 kPa. Followings are outstanding characteristics when silicon single-crystals are used as a density standard.

- (1) Since silicon has near-perfect crystalline structure, its density is extremely stable once it is measured.
- (2) While water and mercury are liquid, and silicon single-crystals are solid, there is much less effect for silicon single-crystals due to degradation of chemical purity and changes in isotropic composition when they are used for calibrating densities of other materials.
- (3) Although the surface is covered with oxide layers, the density of the oxide layers is close to that of substrate silicon single-crystals, and thus the density change due to progressive oxidation is extremely small.

Particularly, (2) is major motivation in promoting the development of a new density standard system replaced from water. Silicon solid density standard is not only highly precise, but it also has excellent usability unseen in the liquid density reference materials in terms of maintenance and management as well as actual operation conducted by the calibration service provider.

3.2 Development of absolute measurement technology for density

Figure 1 shows the laser interferometer developed for absolute measurement of the volume of silicon single-crystals^[31]. Since the size is selected so that the mass of the silicon sphere is to be about 1 kg to realize mass measurement traceable to the Prototype Kilogram of Japan, the diameter is about 94 mm. The volume of the sphere with low sphericity can be calculated accurately from the mean diameter by measuring its diameters from many orientations. Therefore, silicon spheres with a sphericity better than 100 nm are used for the solid density standard.

The SI base unit for length, meter (m), is defined by the speed of light and the wavelength of a light beam determined by

optical frequency measurement, so the frequency of laser source used for the interferometer must be calibrated using the method traceable to the definition of second (s). However, since it is difficult to make absolute measurement of optical frequency each time measurements are made, CIPM set recommended wavelengths of frequency-stabilized lasers where the frequency was absolutely measured beforehand by the method traceable to the definition of second. In the diameter measurement of silicon spheres, we maintain the traceability to the definition of meter by using a laser diode as the light source, whose frequency is calibrated using recommended wavelength of I₂ stabilized He-Ne laser,.

For accurate diameter measurement by optical interferometry, it is important to evaluate the thickness of oxide layers on the sphere surface and to evaluate the phase shift when the incident light beam is reflected on the sphere

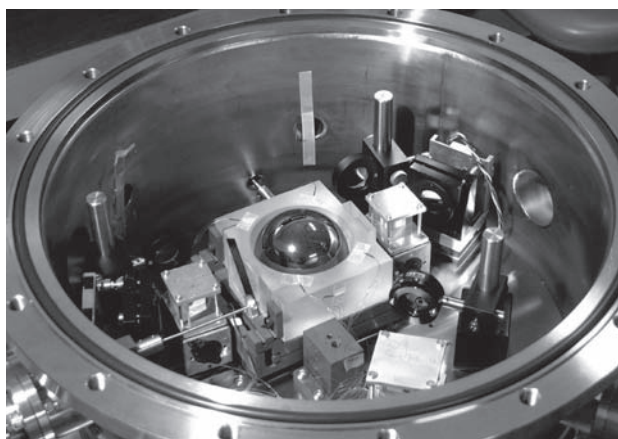


Fig. 1 Laser interferometer for measuring the diameters of silicon spheres.

surface. Particularly, to redefine the SI basic unit, kilogram, by determining the Avogadro constant, the diameter of the silicon sphere must be measured with subnanometer accuracy. The surface of the silicon sphere is normally covered by oxide layers with a thickness of about 3 nm, so it is necessary to implement a surface analysis technology. Traditionally, ellipsometry has been used for silicon spheres, but recently, more accurate and reliable surface measurement techniques are employed using new surface analysis methods such as the x-ray reflectometry (XRR) and x-ray photoelectron spectroscopy (XPS). Since silicon single-crystals have certain coefficient of thermal expansion, it is necessary to measure the sphere temperature with an uncertainty of about 1 mK. Therefore, improvements are made by introducing active radiation shield to realize stable temperature condition in a vacuum chamber.

Table 1 shows the elemental technology for the absolute measurement of the density of silicon single-crystals. To establish the solid density standard traceable to the definition of SI, several measurements standards, such as optical frequency, temperature, surface analysis, and mass are required. The new density standard was built by combining these standards.

3.3 Development of measurement technology for density comparison

To provide traceable hydrometer, density standard liquid, and vibrating tube densimeter to users, new measurement technologies are necessary to compare the densities. Therefore, AIST developed a new hydrostatic weighing apparatus, hydrometer calibration system, and magnetic suspension densimeter as shown below.

Table 1. Elemental technology developed for absolute measurement of density of silicon single-crystals.

Elemental of technology	Development goal	Elemental technology developed to achieve goal
Measurement and control of optical frequency	Nanometre measurement of diameters using gas lasers with fixed frequency (goal when it was impractical to control optical frequency in a wide range)	Modulation and analysis of interference fringe by mechanical scanning of etalon: achieved diameter measurement precision of 3 nm (1994)
	Wideband control of optical frequency and complete automated measurement of diameters by introducing laser diode	Measurement and control of optical frequency at 20 GHz band Complete automated measurement of diameters by the phase shifting method: improved diameter measurement precision to 1 nm (2007)
	Diameter measurement at subnanometre precision	Interference fringe measurement by the dark fringe method: improved performance to the quantum noise limited interferometry (development in progress)
Surface analysis	Evaluation of thickness of oxide layers on the surface of silicon spheres	Spectroscopic ellipsometry of sphere surface (from 1996)
		Combination of XRR and XPS (2007)
Measurement and control of temperature	Precision measurement of temperature of silicon sphere in vacuum	Temperature control of vacuum chamber by circulation of temperature-controlled water: achieved temperature measurement with an uncertainty of 5 mK by evaluating temperature distribution by thermocouples and temperature measurement based on ITS-90 (1994)
		Achieved temperature measurement with an uncertainty of 1 mK by introducing radiation shield and its active temperature control (2008)
Orientation control of sphere	Diameter measurement from multiple orientation in vacuum	Development of automatic control mechanism of orientation of sphere in vacuum and its computer control (1994)
Mathematical derivation of volume	Mathematical determination of volume of imperfect sphere	Establishment of volume derivation method by geometric consideration
Mass measurement	Mass evaluation of silicon sphere in vacuum	Introduction of sinker system for precise air buoyancy correction
		Evaluation of adsorption coefficient at silicon sphere surface

3.3.1 Density calibration of solid material by hydrostatic weighing

Figure 2 shows the structure of hydrostatic weighing apparatus that was developed to calibrate the density of solid materials using silicon spheres^[32]. Tridecane, ($n\text{-C}_{13}\text{H}_{28}$) that has low surface tension and stable density, is used as a working liquid. Density difference is measured with a relative standard uncertainty of 4×10^{-8} by alternately weighing the silicon spheres and the solid sample in the liquid. To correct the effect of density gradient due to temperature distribution and gravity in the liquid, the solid sample is placed between the two silicon spheres placed in vertical direction. This apparatus is now used to calibrate the density of arbitrary solid materials such as stainless steel weight, glass, semiconductor crystal, and precious metals. The density of silicon single-crystals used as secondary standard in JCSS is also calibrated with this apparatus. Figure 3 shows a photograph of the apparatus and density-calibrated silicon single-crystals.

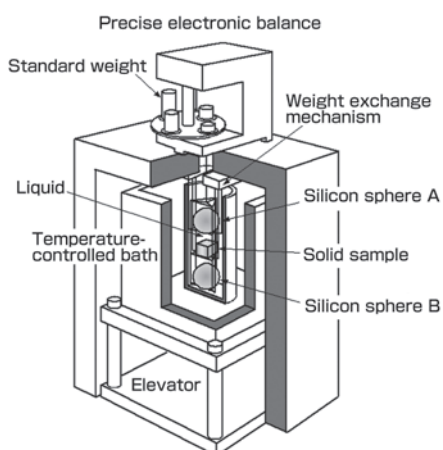


Fig. 2 Structure of hydrostatic weighing apparatus.

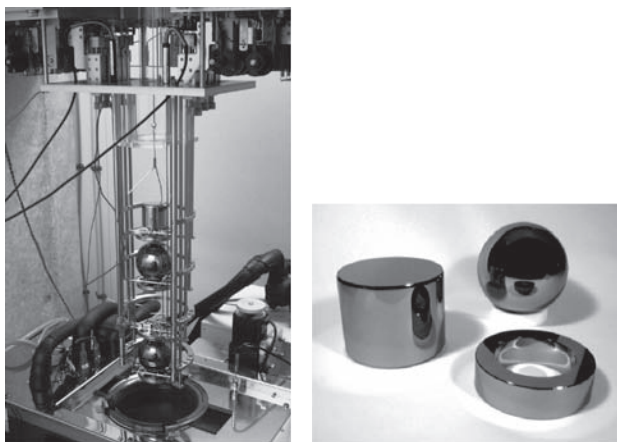


Fig. 3 Hydrostatic weighing apparatus (left) and silicon single-crystals calibrated for density as National Secondary Standard (right). Other than sphere, silicon single-crystals of various forms such as cylinder and ring are used as Secondary Standard.

3.3.2 Hydrometer calibration by the weighing method

Figure 4 shows the principle of scale calibration for hydrometers by hydrostatic weighing. By measuring the buoyancy force acting on the hydrometer in a working liquid using electronic balance, the scale on the stem of hydrometer can be calibrated^[33]. In the conventional weighing method where water was used as the density standard, it was difficult to calibrate the hydrometer scale with a small uncertainty since the surface tension of water is high and sensitive to surface contamination. Currently, tridecane is used as the working liquid instead of water. Therefore, the method involves calibrating the density of tridecane by hydrostatic weighing using a ring-shaped silicon single-crystals with calibrated density (National Secondary Standard). It measures the density of the working liquid near the body of the hydrometer. Standard Instrument Testing according to the Measurement Law and hydrometer scale calibration in JCSS are conducted using this method.

3.3.3 Calibration of density standard liquid using magnetic suspension densitometer

Vibrating tube densimeters^[34] are used in various fields including petroleum, alcohol, brewing, food industries, as well as for medical testing as a high-sensitivity density measuring device. Normally, since calibration is done using only water and air as the density reference materials, the uncertainty of the density measurement is relatively large when used in a range that departs from the density of the reference materials. Therefore, reliability and traceability of the vibrating tube densimeters can be maintained by supplying several density standard liquids in a range of about 0.5 g/cm^3 to 2.0 g/cm^3 .

Figure 5 shows the magnetic suspension densitometer developed at the AIST to calibrate the density standard liquids^[35]. This densitometer measures density of fluid according to the same principle as the hydrostatic weighing shown in Figure 2. Since it uses non-contacting mechanism

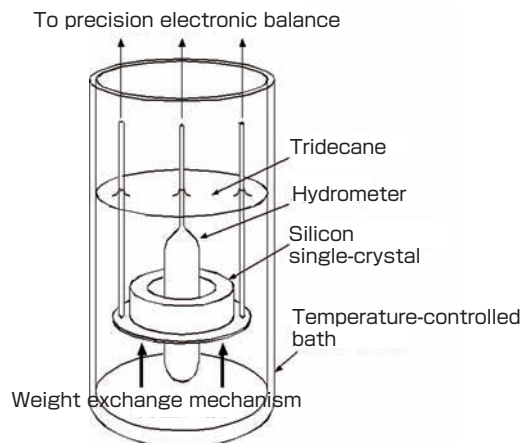


Fig. 4 Ring shaped silicon single-crystal used for calibrating hydrometers.

using magnetic suspension, it can measure the density of fluids under high-pressure and liquids with high vapor pressure without influence of surface tension at meniscus.

By using silicon single-crystals as a sinker, and calibrating its density by hydrostatic weighing, traceable density standard liquids can be supplied in a wide temperature and pressure range. The relative standard uncertainty of the density standard liquids calibrated by this principle is 7×10^{-6} . The measurement result at AIST is used as a reference value when conducting performance test to verify the correctness of measurements of registered calibration service providers of JCSS.

4 Investigation for uncertainty and international equivalence

As mentioned in Section 3.2, in Japan, the density of silicon spheres is determined by absolute measurements of their diameters and masses, and they are designated as the National Primary Standard of density by Measurement Law. The values of the National Primary Standard and uncertainty are shown in Table 2. This is based on the absolute measurements of the density conducted by AIST until 2005, and the relative combined standard uncertainty of the density is 1.2×10^{-7} .

To verify the correctness of the absolute values and uncertainty of Japanese solid density standard and to

confirm the international equivalence are important issues in advancing MRA of measurement standard and to demonstrate the reliability of Japanese density measuring instruments. Therefore, the author distributed questionnaires to national metrology institutes of various countries and surveyed the density calibration method and the status of density reference in each country as key comparison study for the Working Group on Density of the CCM. As a result, it was found that although there were very few national metrology institutes that have independent standard for absolute value of density like AIST, many countries have already started to establish traceability based on solid density standard such as silicon single-crystals instead of water. In this key comparison, designated as CCM.D-K1, a silicon sphere of NMIJ was transported to participating countries from 2001 to 2002, to evaluate the international equivalence of the density standards. The participating countries measured the density of the silicon sphere by hydrostatic weighing and the values were compared.

The measurements at national metrology institutes of eight countries including NMIJ are shown in Figure 6. The value of NMIJ showed smallest uncertainty, and the values of other participating countries fell in the range of uncertainty. The reference value calculated from the weighted mean of these values is most reliable as an absolute density value traceable to the definition of SI. The value of NMIJ agrees very well also with the reference value. This verifies the high reliability of the absolute and relative density measurements conducted at the NMIJ.

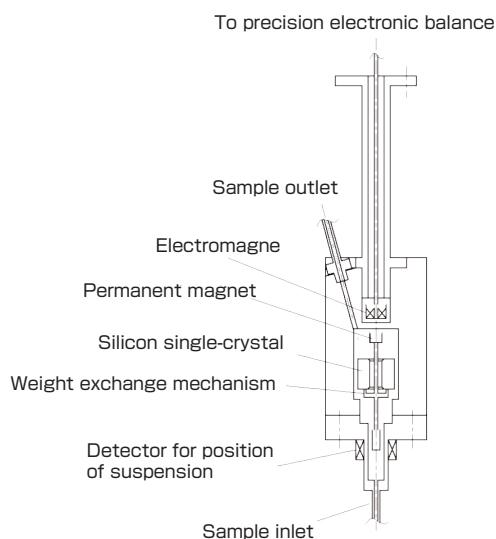


Fig. 5 Magnetic suspension densitometer.

Table 2. Absolute values of the volume, mass, and density of Primary Standards S4 and S5 at 20 °C and 101.325 kPa.

Physical quantity	Unit	Sphere S4	Sphere S5	Relative combined standard uncertainty $u_{rel}/10^{-6}$
Volume	cm ³	429.601242	429.615 387	0.119
Mass	g	1000.578 619	1000.612 019	0.016
Density	kg·m ⁻³	2329.086 89	2329.087 95	0.120

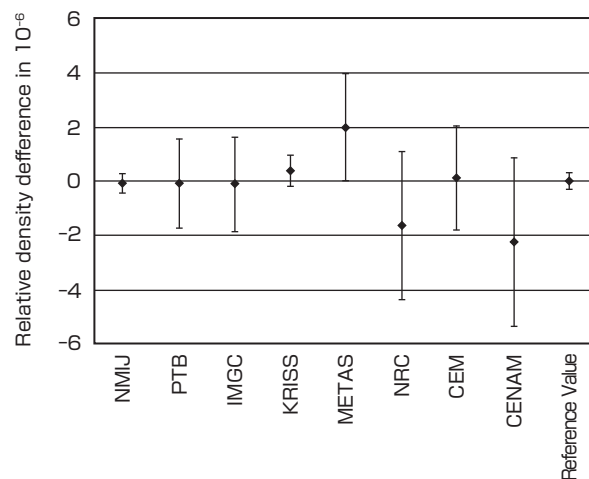


Fig. 6 Measurement result of the key comparison CCM. D-K1 organized by the Working Group on Density of the CCM, CIPM. A 1 kg Silicon sphere was transported as a travelling standard to NMIs of participating countries, and the density of the travelling standard was measured using hydrostatic weighing apparatus using solid density standard of the participating institute. Error bar expresses the expanded uncertainty ($k=2$). Participating metrological institutes were NMIJ (Japan), PTB (Germany), IMGC (Italy, currently INRIM), KRISS (Korea), METAS (Switzerland), NRC (Canada), CEM (Spain), and CENAM (Mexico). Reference value is the weighted mean of measurements of all participants.

For the density standard liquids, key comparison CCM.D-K2 lead by the Working Group on Density of the CCM was conducted and completed in 2005. International equivalence for the calibrations at the NMIJ was thus verified also in this key comparison.

5 Establishment of traceability system for density and contribution to society

AIST cooperated with the National Institute of Testing and Evaluation (NITE), which is the accreditation body of JCSS, since 2000, and started creating guideline for technological application necessary for implementing calibration service for density based on ISO/IEC 17025 standard. This guideline describes the methods for: maintaining traceability from silicon spheres designated as the National Primary Standard; calibration method of hydrometer, density standard liquid, and vibrating tube densimeter, and the frequency of calibration. Considerations and investigations were conducted as joint work with several candidate calibration service providers. In preparing the guideline, as much freedom as possible was given to the calibration system built by registered calibration service providers, while ensuring accurate evaluation of the uncertainty of the calibration, to allow evolution of density calibration service into various forms in the future. From 2001 when the first technological application guideline for the density calibration service was set up, AIST personnel cooperated as technical advisor in the certification process conducted by NITE.

Figure 7 shows the traceability system constructed on the absolute and comparative measurements for density. The silicon spheres S4 and S5 for which the absolute measurement of density were conducted are set at the top of traceability (National Primary Standard), and silicon single-crystals calibrated by hydrostatic weighing (see Figures 2 and 3) are used as the Secondary Standard at the registered

calibration service. In JCSS, registered calibration service provider that fulfilled the ISO/IEC 17025 standard may use the Secondary Standard to calibrate the users' measurement instruments such as hydrometer, density standard liquid, and vibrating tube densimeter.

The number of provision of density standard by JCSS increased drastically since 2001, and in 2007, about 6,000 calibration certificates were issued for a year for users' density measuring instruments. Particularly, for alcohol concentration measurement of alcoholic beverages, "measurement of alcohol concentration using vibrating tube densimeter" was conventionally approved for use as "method that is deemed practical and accurate, although it is listed in the Official Analysis Method of the National Tax Agency," and application to the National Tax Agency was required to use the vibrating tube densimeter. Also, for alcohol table to convert density to alcohol concentration, values were provided by the Official Analysis Method, and it was necessary for AIST to compare the values with the alcohol table used in Measurement Law before introducing the vibrating tube densimeters calibrated according to JCSS for use in assessing alcohol tax. Therefore, AIST collaborated with the National Tax Agency and disclosed the alcohol table used by AIST on the website, and the people in the brewing industry can readily refer to the AIST alcohol table. It was now possible to use the alcohol concentration measured by the vibrating tube densimeters calibrated according to JCSS as basis of tax assessment by Alcohol Tax Law. Hence, vibrating tube densimeters came into wide use, and in 2007, the National Tax Agency decided to deregulate, and "measurement of alcohol concentration by the vibrating tube densimeter" was included in the Official Analysis Method. As long as the vibrating tube densimeters are calibrated by the density standard liquids provided by the registered calibration service certified by JCSS, it may be used for measurement of alcohols concentration for tax assesment. The Japanese government thus recognized the reliability of the densimeters approved by JCSS, and the use in the brewing industry is increasing steadily.

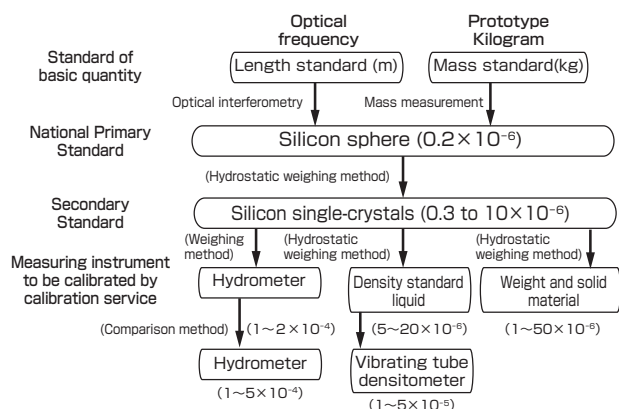


Fig. 7 Traceability system with density of silicon sphere at the top.
Values in parentheses show the estimated relative expanded uncertainty at 95 % confidence level.

6 Development into new measurement evaluation technology

The comparative measurement technology for density employed by JCSS is described in Section 3.3, and AIST is developing other new density comparison technologies for material science and energy conservation. Comparison of the densities between silicon single-crystals using the pressure-of-flotation method^[36] is a technology originally developed to improve the accuracy of the Avogadro constant. It detects very small density distribution in the crystal, and now it is applied to density measurement of thin films^[37], since the measurement sensitivity is extremely high and can detect a relative density difference of 10⁻⁷ to 10⁻⁸. The density of thin

films with 10 to 100 nm thickness formed on silicon substrate is successfully measured with a relative uncertainty of about 0.1 %. Using this principle, it became possible to evaluate the density of oxide films that are vapor-deposited by different methods, and to specify a particular film manufacturing condition that gives highest density for the oxide films^[38].

Moreover, improvements were made to the magnetic suspension densitometer mentioned in Section 3.3.3, and a new PVT property (pressure-density-temperature relation) measurement technology was developed at the AIST^[39]. It cancels out the effect of diamagnetism of the sample fluid itself near-completely. This new magnetic suspension densitometer employs dual sinkers using germanium single-crystals that has different density from that of silicon single-crystals. They are used as sinkers, and measurements of PVT properties for working fluids and alternative refrigerants are being conducted with high accuracy.

Table 3 shows the examples of application of these measurement technologies used in the silicon density standard. They were created only after the density standard using silicon single-crystals became available, and it would have been extremely difficult to develop them from a standard system based on water.

7 Conclusion

Since silicon single-crystals with near-perfect crystalline structure have excellent properties such as form stability and density stability, it can be used as the material for the solid density standard. AIST developed the technology for the absolute measurement of density from diameter and mass measurements of silicon spheres, and constructed a new density standard system replaced from water, through integration of comparative measurement techniques of density. These density measurement technologies were not only employed in the Standard Instrument Testing and certification according to Measurement Law, but also realized the traceability of the density measurement in JCSS. It is now

contributing to maintenance of traceability for densimeters used in industry. The number of calibrations of density measuring instruments by JCSS is thus increasing steadily.

Future issue is to advance this solid density standard system by integrating it with new evaluation technologies for material science and thermophysical properties, and to actively apply them for semiconductor industry and energy conservation.

Acknowledgement

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Terminology

Term 1. Relative combined standard uncertainty: The concept that expresses the quality of measurement was formerly called error. It is now summarized in the *Guide to the Expression of Uncertainty in Measurement* in ISO/IEC. The standard uncertainty of a quantity x is expressed as $u(x)$ which is the variation in measurement of a certain quantity x , and it is determined by the standard deviation of the measurement. The relative combined standard uncertainty $u_{c,r}(y) = u_c(y)/y$ is expressed as a relative quantity of the combined standard uncertainty $u_c(y)$ where the standard uncertainties of multiple input parameters are combined by error propagation equation.

Term 2. MRA (Mutual Recognition Arrangement): In measurement standard, the equivalence of standard provided by the national metrology institutes (NMIs) of countries or regions is mutually recognized, and calibration certificates issued by the NMIs are mutually recognized. The measuring instrument calibrated by a certain NMI can be used in other countries or regions without recalibration, to ensure one-stop service for users. Based on the TBT agreement, transparency in imposing mandatory regulation, voluntary regulation, or compatibility evaluation procedures is maintained, and international accord is promoted by international

Table 3. Development and application of new measurement technology for density comparison.

Measurement method	Characteristics	Examples for application
Pressure-of-flotation method	Detection of small density difference among silicon samples Uncertainty of measurement of relative density difference is 10^{-7} to 10^{-8} Require extremely precise temperature control (10 to 100 μ K)	Evaluation of density distribution in silicon crystals Evaluation of defect in silicon crystals
	Density measurement of thin films	Evaluation of thin film manufacturing process Evaluation of density of SAW device Evaluation of density of flexible print substrate
Magnetic suspension method	Precise measurement of PVT properties	Density measurement of gas and liquid
	Possible to measure density by cancelling out the effect of diamagnetic properties of fluids with unknown magnetic susceptibility Employ double sinker method with silicon and germanium single-crystals	Evaluation of thermophysical properties of working fluids and alternative refrigerants Development of energy conservation technology Protection of earth environment Control of carbon gas emission

standards and international guidelines to remove as much as possible the standards and certifications that may remain as trade barriers.

- Term 3. Traceability: This is a general term for measurement management system where the chain of comparisons (calibrations) using international and national standards reaches the measuring instrument at user level. In ISO/IEC 17025 standard, primary standard realized according to the definition of the International System of Units (SI) must be used at the top of traceability.
- Term 4. Japan Calibration Service System (JCSS): This originated as Japan Calibration Certification System for calibration service providers according to Measurement Law in November 1993. In July 2005, it became a system to register calibration service providers after screening them for compatibility with requirements for testing and calibration laboratories (ISO/IEC 17025) set by International Organization for Standardization (ISO) and International Electrotechnical Commission (IEC).
- Term 5. ISO/IEC 17025 standard: International standard document on quality control for services provided by testing and calibration laboratories. Physical standards provided by NMIJ, AIST are subjected to quality control and third-party verification based on this standard.

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Discussion with Reviewers

1 On manufacture of sample and importance of evaluation Question (Norimitsu Murayama)

The success of this research was achieved by successful manufacture of high-quality silicon single-crystal sphere, along with development of various elemental technologies for absolute measurement of density. I think the synthesesiological value of this paper will increase if you describe the manufacturing process and quality evaluation (purity, crystal imperfection, and etc.) of the silicon sphere.

Answer (Kenichi Fujii)

Since development of technology to polish silicon single-crystals into 1 kg sphere with high sphericity by CSIRO of Australia was major motivation for establishing new density standard to replace water, I added the manufacturing procedure and quality evaluation to the beginning of Section 3. Also, I added Reference [26] for details of polishing method. If the sphere was to be used only for density standard, it was not important to evaluate the purity or defect in the silicon spheres, and it would have been sufficient simply to guarantee the stability of the density by measurement. However, for determining the Avogadro constant, it was essential to correct the effect of impurities on density and lattice constant, to quantify the concentration of defects and atomic vacancies, and to accurately evaluate the average number of atoms in the unit cell. If the sphere was polished by conventional mechanical polishing, crystal defects occurred near the surface and it would be difficult to accurately determine the Avogadro constant. Therefore, CSIRO employed a mechano-chemical polishing method that incorporated chemical polishing at the final phase of polishing to minimize the subsurface damage in the crystal. By taking such polishing process, not only geometric perfection of the sphere, but also the crystallographic perfection can be guaranteed.

2 Technical terminologies

Question (Norimitsu Murayama, Mitsuru Tanaka)

I think readers from other fields will be able to understand better if you provide definitions and concepts for “relative combined standard uncertainty” and “the standard traceable to the definition of SI.”

Answer (Kenichi Fujii)

I added a Terminology section after Acknowledgements to explain relative combined standard uncertainty and traceability.

3 Scientific demand

Question (Mitsuru Tanaka)

The description about demands in fundamental physical constants in 2.2 Scientific demand does not necessarily cover scientific demands, so I think you should give other examples. Perhaps you may discuss “verification of theory for the von Klitzing constant R_K (or the fine structure constant α).”

Answer (Kenichi Fujii)

I added importance of verification for theories used in the Josephson and quantum Hall effects as scientific demand for measuring the Avogadro constant in Section 2.2.

4 Scientific issues to be positioned as Type 1 Basic Research that composes Full Research

Question (Mitsuru Tanaka)

The study to determine the Avogadro constant by silicon single-crystals is described as starting point. Rather, it may be easier for people to understand, if volumetric technology of sphere is set as *Type 1 Basic Research*. Since scientific output is included as goal of *Full Research*, I think it makes it difficult to understand if you start from determination of the Avogadro constant from

silicon single-crystals.

Answer (Kenichi Fujii)

For *Type 2 Basic Research* scenario, when we started research to improve uncertainty of volumetric technology for spheres around 1984, it was necessary to conduct volume measurement of quartz spheres for absolute measurement of the density of water that was being conducted at the former National Research Laboratory of Metrology. While the volumetric accuracy needed for this study was about 10^{-7} , the reason for obtaining volume at higher accuracy was to improve the uncertainty of the Avogadro constant. Although development of volumetric technology required for density standard can be considered *Type 1 Basic Research*, the reason for improving volumetric accuracy to 10^{-8} was the development of polishing technology for silicon spheres at the CSIRO in 1987, and this development was also aimed at improving the uncertainty of the Avogadro constant.

5 Description of *Product Realization Research* in society and industry

Question (Mitsuru Tanaka)

The Author contributed greatly to the dissemination of research result through instructions to registered calibration service providers, certification process, and creation of

technological standard for certification. I think you should also mention the relationship between the AIST's advice and the National Tax Agency's notification on alcohol table. Also, I think you should include international activities such as the Working Group on Density of the CCM.

Answer (Kenichi Fujii)

In Section 4, I added that the author et al conducted CIPM key comparison for density for first time in the world to verify the international equivalence of the density standard, as well as our contribution to activities in the WGD/CCM/CIPM.

In Section 5 Establishment of traceability system for density and contribution to society, I added our contributions including technical advice to registered calibration service providers, work on JCSS certification process, and creation of technology standard of JCSS certification. Much time were spend on these activities, and I held several meetings and sessions to make sure people working on calibration services would correctly understand the key points in conducting traceable measurement. Also, talking to the people in calibration service was extremely useful opportunity to know which technologies and information were desired by end users, and I think this is important process for AIST to make contributions to the society.

A rationalization guideline for the utilization of energy and resources considering total manufacturing processes

— An exergy analysis of aluminum casting processes —

Hideki Kita^{*}, Hideki Hyuga, and Naoki Kondo

[Translation from *Synthesiology*, Vol.1, No.3, p.212-221 (2008)]

In order to increase manufacture efficiency and lower environmental impact, it is necessary to know the processes of consumption and emission of resource and energy, as the processes span out widely after originating from one process. In this paper, analysis and comparison of exergy were conducted in case when heater tube used in the molten aluminum was made of steel and ceramics. Exergy analysis was done for complete operation of aluminum casting. We then created a guideline for rationalization of casting process for efficient use of resource and energy.

Keywords : Exergy, environment, manufacturing, system, efficiency, rationalization

1 Introduction

“Manufacturing,” where useful products are obtained by processing raw material, is a system that converts resource that originally exists in nature into matter and energy in useful form, while it also releases useless substance and energy into the environment. Manufacturing is a series of processes starting from mining, transportation, use, and disposal. It is an assembly of subsystems of individual processes. The product becomes useless with passage of time and is disposed, and returns to the environmental though it takes considerable amount of time. In the expanse of space and time, all systems related to manufacturing affect the environment, as matter and energy are exchanged with the surrounding environment while maintaining mutual relevance (Figure 1).

During the period of rapid economic growth in Japan in the 1960s, orientation of manufacturing was mass production and mass consumption, and waste could be buried. Today,

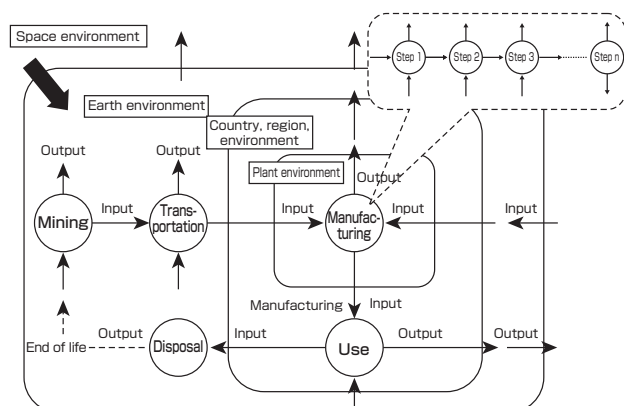


Fig. 1 Relationship between manufacturing system and environment.

environment and economy must both be sustained, and uncontrolled consumption and emission from individual systems cannot be allowed, although problems cannot be solved simply by optimization, sizing down, or combination of the two. It is normal for individual and group to be in conflict, and a manufacturing system that seems to consume only small amount may have underlying system of large consumption and emission, and the load may increase in total sum. To reduce consumption and emission as total while maintaining competitive edge, it is necessary to know the process of consumption and emission that originates from individual and spreads out to entirety, to clarify its size and significance, and to strategically utilize this knowledge. In this paper, we decided to consider exergy as main concept for both evaluation and development. Exergy is Gibbs free energy based on environment, and is defined as maximum work that can be achieved until system and environment reach thermal equilibrium^{[1]-[3]}.

Exergy is consumed unilaterally through production activities, and is a suitable indicator to quantify resource consumption level that is common to matter and energy. By using exergy, it is also possible to clarify the energy value of things and input and output energy in the cycle, as well as theoretical limit. It can be used to set guideline for rationalization of process. Although it is important to evaluate the situation using exergy as index, this alone will not cause any revolution. We believe it is necessary to present rational hardware and process that are useful in mitigating environmental impact and resource consumption while linking evaluation result with development, and presenting them as new value where environmental impacts are reduced at wide-ranging levels (Figure 2).

Exergy is described as measure of efficient use of heat

according to JIS^[4], and has been used as guideline for heat engines and architectural designs^{[2], [5]-[7]}. In the manufacturing field, it is used in rationalizing iron and steel making and chemical processes, but there was no case that addressed resource consumption process or rationalization guideline for system in which manufacturing of different fields are integrated. In this paper, exergy analysis was conducted for use and disposal of ceramics and steel members, and when these were used as production members in aluminum casting line for engine parts. First, we looked at the point where consumption and emission of exergy are in conflict depending on the definition of “boundary” such as operation, manufacture, and use, and attempted clarify the significance and scale of consumption process. Based on this analysis, we then created a guideline for process rationalization.

2 Analysis method

2.1 Calculation of exergy

① Chemical exergy of matter^[1]

If reference compound has composition $X_xA_aB_b \dots$ (X, A, B are elements; x, a, b are composition ratios), is produced by chemical reaction (1), and change of Gibbs free energy is ΔG^0 , then chemical exergy E_x^0 can be calculated by equation (2).



$$E_x^0 = \frac{1}{x} [-\Delta G^0 - aE_x^0(A) - bE_x^0(B) - \dots] \quad \dots (2)$$

Reference material is matter that does not chemically react alone in an environment, and its exergy is zero according to the definition. Reference materials are listed in JIS^[4], but for unlisted materials, we set the material with lowest free energy as reference material.

② System accompanying chemical reaction^{[5][7]}

The value of free energy available as thermodynamic data is mostly value at standard condition, i.e. 1 mol of pure material, and adjustment is necessary in exergy calculation. Reactant r_1 is matter that does not exist in surrounding environment, while reactant r_i ($i = 2, 3, \dots L$) and product p_j ($j = 1, 2, \dots N$) are matters that exist in surrounding environment. Molar fractions of reactant r_i and product p_j

are x_{r_i} and x_{p_j} respectively, and their molar fractions differ according to the surrounding environment. Also n_{r_i} and n_{p_j} are quantities of material (mol) of reactant and product respectively.

$$\left(\sum_{j=1}^N n_{p_j} RT_0 \ln \frac{1}{x_{p_j}} - n_{r_1} - \Delta G - \sum_{i=2}^L n_{r_i} RT_0 \ln \frac{1}{x_{r_i}} \right) + \sum_{i=2}^L n_{r_i} RT_0 \ln \frac{x_{r_i}}{x_{r_i}} - S_g T_0 = \sum_{j=1}^N n_{p_j} RT_0 \ln \frac{x_{p_j}}{x_{p_j}} \quad \dots (3)$$

The first section in [] on left side of the equation shows the chemical exergy of reactant r_1 . The second section on left side is separation exergy when reactant r_i ($i = 2, 3, \dots L$) has molar fraction x_{r_i} , and first section on right side is separation exergy when product p_j ($j = 1, 2, \dots N$) has molar fraction x_{p_j} . Also, S is entropy, T_0 is environmental temperature (K), and R is gas constant.

③ Organic material

Although equations of Rant^[8] and Szarut^[9] are known for calculation of chemical exergy for organic material, we used the following equation^[10] derived by Nobusawa et al who modified the equations for practical use.

$$E_x = m \cdot H_l \cdot [1.0064 + 0.1519 \frac{\phi_H}{\phi_C} + 0.0616 \frac{\phi_O}{\phi_C} + 0.0429 \frac{\phi_N}{\phi_C}] \quad \dots (4)$$

m and H_l are dry mass (kg) and lower heating value (J/kg) of organic compounds respectively. ϕ_C , ϕ_H , ϕ_O , and ϕ_N are weight fractions of carbon, hydrogen, oxygen, and nitrogen in the organic compound.

④ Electric power and gas fuel

Electric power is energy that does not contain entropy, so it was used as value for exergy. On the other hand, exergy of fuel gas was calculated using the following equation^[10].

$$e^0 = \sum x_i e^0 + R_i T_0 \sum x_i \ln(x_i) \quad \dots (5)$$

e_i is exergy and superscript 0 indicates standard temperature (25 °C), and subscript i is for ingredient i . x_i is volume fraction of ingredient i .

2.2 Organization of system and input/output data

In this paper, overall composition in manufacturing is called “system,” and mining, transportation, use, and disposal

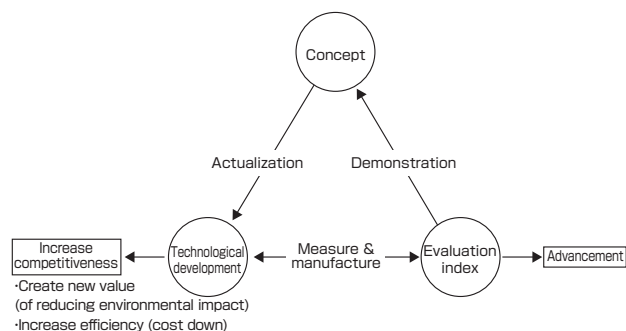


Fig. 2 Importance of linkage between technology and index.

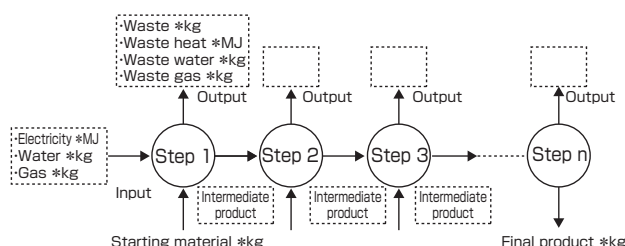


Fig. 3 Input-output and flow to operation.

are called “processes.” The process is aggregation of “operations.”

Figure 3 shows the input/output flow of matter and energy during operation. While raw fuel is introduced and intermediate product is produced for each operation, waste material and heat are also produced and these are emitted outside the system. The intermediate product becomes raw material for the next operation, and final product is made after series of operations.

To calculate exergy, it is necessary to know the type and the quantity of all raw materials and energies that are introduced into and emitted from the operations, from material to final product. In this study, we were able to obtain data in actual manufacturing by cooperation of major manufacturer. In most cases, we used data while some parts were unknown, and unknowns were filled in with estimate values based on experience.

2.3 Manufacturing efficiency

The percentage of exergy of product against sum of exergies of all input fuel and energy was called fixed ratio of exergy within members (η).

$$\eta = E_x(p) / E_x(in) \quad \dots\dots (6)$$

Here, $E_x(p)$ is chemical exergy of product, and $E_x(in)$ is sum of input exergies. In this paper, we evaluated manufacturing efficiency by considering both fixed ratio of exergy within member and exergy needed for input.

3 Case study

3.1 Aluminum casting line operation and role of heater tube

Aluminum has excellent heat conductivity and is lightweight, and therefore is used widely in engine parts. Also, aluminum is highly recyclable, so disposed engines are collected as scraps and recycled as engine after undergoing some processes. Figure 4 shows the recycling system mainly for aluminum casting line operation. First, recovered waste engine (scrap) are melted in centralized furnace. They are

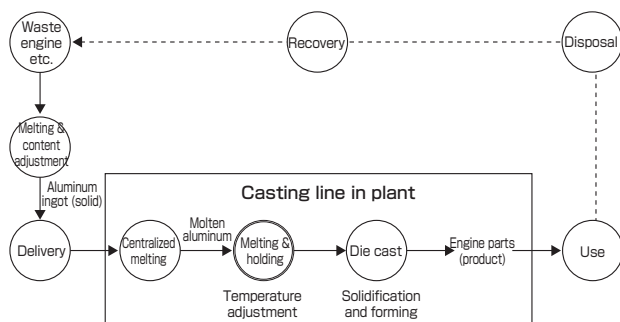


Fig. 4 Aluminum cycle and casting line operation.

made into solid ingots, delivered within the plant, melted again in centralized furnace, and then transferred to holding furnace. The molten metal is adjusted for temperature and content, distributed to die cast machine, and formed into products. In this cycling system, there are many factors that decrease efficiency including heat loss, oxidation of molten aluminum, and inclusion of impurities. Input of energies and things from outside is unavoidable to maintain certain quality level and production volume, and reducing these inputs is expected to increase the efficiency of the cycling system.

As one of measure, use of ceramics in production member has been attempted. Heater tube (Figure 6) used in holding furnace (Figure 5) is one example. It is a protective tube that envelops the heating wires, and is used to maintain constant temperature of molten aluminum. Heat efficiency increases by using highly conservative silicon nitride, which allows horizontal dip structure where the tube is fixed horizontally in the bottom of the furnace (Figure 5). However, ceramic tube is much more expensive than iron tube. We conducted exergy analysis for manufacture-use-disposal in cases where the heater tube (weight 19 kg) was made with silicon nitride and when it was made with iron^{[11][12]}.

3.2 Calculation of chemical exergy

In conducting the analysis, it is necessary to calculate the exergies of all materials involved in the manufacture. The process of calculation of exergy is shown using silicon nitride (Si_3N_4), the main material. The reference material of silicon nitride is silica and air.

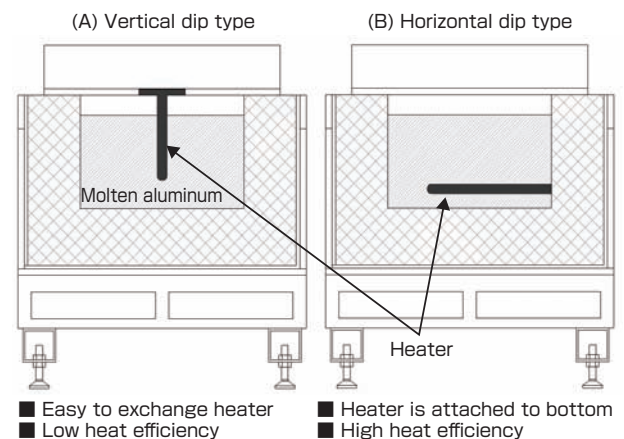


Fig. 5 Structure of holding furnace.

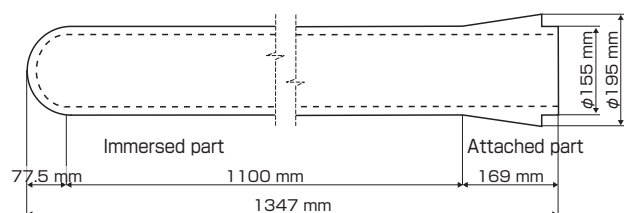


Fig. 6 Form and dimensions of heater tube.

$$E_x(N_2) = RT_0 \ln(101.3/76.57) \quad \dots\dots (7)$$



$$E_x(Si) = (-\Delta G^0) + E_x(SiO_2) - E_x(O_2) \quad \dots\dots (9)$$

$$E_x(Si_3N_4) = 3(\Delta G^0) + 3E_x(Si) + 2E_x(N_2) \quad \dots\dots (10)$$

$E_x(Xi)$ shows the exergy for material Xi. The section in parenthesis in equation (8) is ratio of total pressure of air and partial pressure of nitrogen. From the above equations, exergy of silicon nitride was calculated to be 1877 kJ/mol. Using similar method, exergies values for major fuels were calculated (Table).

Table. Calculation of exergy for related main fuel.

Raw material and fuel	Exergy
Y ₂ O ₃	47 kJ/mol
Al ₂ O ₃	0 kJ/mol
Si ₃ N ₄	1877 kJ/mol
N ₂	7×10 ⁻¹ kJ/mol
Fe ₂ O ₃	0 kJ/mol
Si	851 kJ/mol
Fe	368 kJ/mol
Al	788 kJ/mol
CO ₂	20 kJ/mol
O ₂	4 kJ/mol
PVA	49 MJ/kg
LPG	48 MJ/kg

3.3 Consumption and efficiency by operation

Figure 7 shows the values of exergies that come in and go out throughout manufacturing operation of silicon nitride member and during complete manufacturing. The silicon nitride material is input to this system as artifact made by melting and reducing silicon oxide at a different plant and then reacted with nitrogen. The exergy of material was calculated as 291 MJ for one product. The product begins as starting material in powder form, and is created by mixing, granulation, forming, dewaxing, and sintering. Looking at each operation, large exergy is required for granulation and sintering of 2547 MJ and 776 MJ, respectively, and this is about 80 % of all exergy input. It was found that these were almost entirely emitted outside the system as waste heat, while powder raw material was collected and there was almost no loss between the operations. Exergy fixed in final product was 229 MJ, and this was only 5.5 % of exergy input (4175 MJ). This was an extremely inefficient process where 94.5 % or 3946 MJ was disposed.

material is iron oxide (Fe₂O₃) whose exergy is 0 by definition. It was manufactured by effectively utilizing the reaction of material such as reduction, and was found that exergy input and output at all operations was small and equalized. Exergy fixed in product was 126 MJ, which was about 20 % of exergy input (621 MJ), and the amount of exergy input was extremely low, about 1/7 compared to ceramics. Therefore, looking at the system of manufacturing one product, it was confirmed that ceramics consumed significantly higher amount of exergy compared to steel, and efficiency was low.

3.4 Exergy analysis at each process

3.4.1 Use

①Wear and material disposal

When steel heater tube is used in molten aluminum, it is corroded by aluminum and worn down by passage of time *t*. It was assumed that wastage progressed according to the following equation.

$$D=D_0 \cdot (2-\exp(kt)) \quad \dots\dots (11)$$

Figure 8 shows the input-output of exergy by operation in manufacturing using steel member. In case of steel, starting

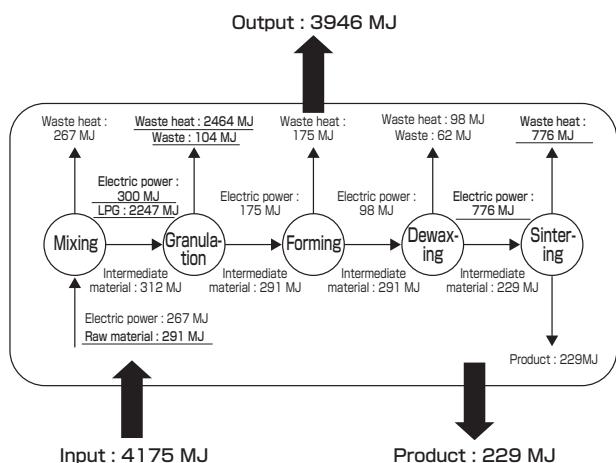


Fig. 7 Operations for ceramics parts and exergy balance during manufacture (for one product with weight 19 kg).

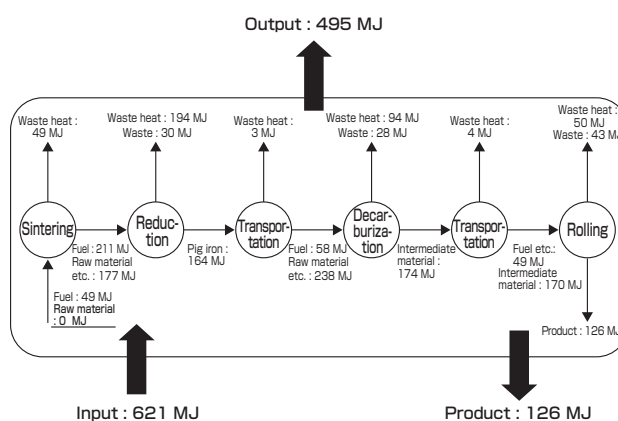


Fig. 8 Operations for steel parts and exergy balance during manufacture (for one product with weight 19 kg).

Here, D is thickness of heater tube (mm), D_0 is initial thickness (mm), k is apparent reaction speed coefficient, and D_i is thickness at time of replacement (mm). Assuming $D_0 = 3$ mm (from data) and $D_i = 0.5$ mm, under condition of replacement every half year, the reaction constant k was calculated to be 0.067578.

Consumption exergy is expressed by following equation.

$$E = E_0 \cdot \exp(kt) \dots\dots (12)$$

Exergy of steel is 6.6 MJ/kg (= 368 KJ/mol) and total weight of the product is 19 kg, and when it is disposed when damage reaches D_i , consumption is 126 MJ/tube. While steel heater tube is exchanged once every half year, silicon nitride is stable and does not react, and is exchanged and disposed along with furnace that has lifespan of 7 years. Figure 9 shows the change with time of exergy consumption in 7 years. Exergy consumed by disposal during this time is as shown in the following equation.

- Steel: 126 (MJ/tube) × 14 (tubes) = 1764 MJ
- Silicon nitride: 229 (MJ/tube) × 1 (tube) = 229 MJ

When steel heater tube is used, damage and disposal are repeated and exergy consumption increases in step-like form. In contrast, there is hardly any consumption in 7 years using ceramics, and exergy value (229 MJ) is released at the end of furnace lifespan. Also, using ceramics, there is less chance of inclusion of impurities compared to steel, so clean molten metal can be obtained, and this is another advantage of ceramics.

②Running

(a) Melting and holding furnace

In vertical dip type using steel heater tube, 9.4 kW is required during run and 4.0 kW at rest, while in horizontal dip type using silicon nitride, electricity consumptions at run and rest are 6.8kW and 3.8 kW respectively, due to improved heat efficiency. While it will be running 60 % (40 % rest) per day and is in operation 360 days a year, the total electricity

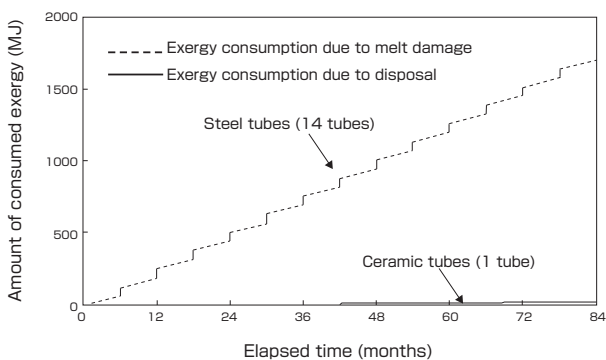


Fig. 9 Comparison of exergy consumption due to melt damage and disposal during use (calculation for 7 years).

consumed in 7 years, or exergy input, will be as follows.

- Steel: $(9.4 \times 0.6 \times 24 + 4.0 \times 0.4 \times 24) \times 360 \times 7 \times 3.6/1000 = 1576$ GJ
- Silicon nitride: $(6.8 \times 0.6 \times 24 + 3.8 \times 0.4 \times 24) \times 360 \times 7 \times 3.6/1000 = 1219$ GJ

(b) Die cast machine

Assuming that electricity consumption of die cast machine is 20 kW, running 60 % per day for 360 days per year, the total electricity consumption, or exergy input, for 7 years is as follows.

$$20 \times 0.6 \times 24 \times 360 \times 7 \times 3.6/1000 = 2612$$
 GJ

3.4.2 Manufacture, use, and disposal

As result of interview with companies, the total manufacture volume of cast product in 7 years was estimated to be about 4300 ton. In this paper, material loss is not considered. Therefore, the amount of molten aluminum is 4300 ton or same as final product, and the exergy was calculated as 126802 GJ in molten condition (temperature 700 °C), and 125582 GJ in solid condition.

Figure 10 shows the amount and flow of exergy input and output for manufacture using ceramics and steel heater tube, their use in melting and holding furnace when casting was conducted for 7 years. As mentioned above, when the furnace is run for 7 years, 14 steel tubes are required since they are subject to damage. Therefore, energy input and output during the manufacture process is as follows.

- Input: 621 (MJ/tube) × 14 (/tubes) = 8694 MJ
- Output: 495 (MJ/tube) × 14 (/tubes) = 6930 MJ

On the other hand, only one silicon nitride tube is required during same time, and exergy for input and output will be 4175 MJ and 3946 MJ respectively according to Figure 7. Next, exergy accompanying damage and disposal during use is as follows.

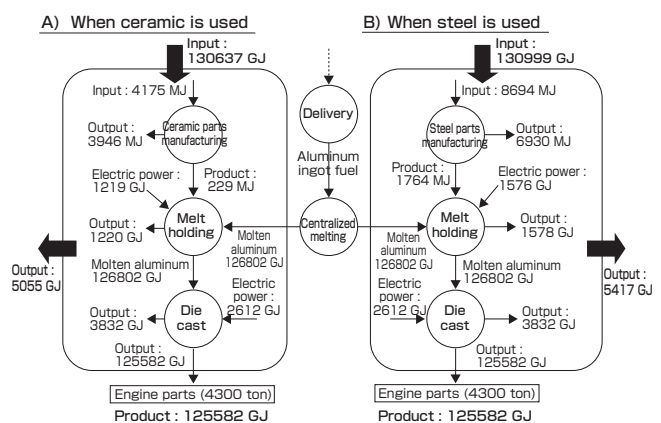


Fig. 10 Exergy balance in casting aluminum engine parts (7 years).

- Steel: $126 \text{ (MJ/ tube)} \times 14 \text{ (tubes)} = 1764 \text{ MJ}$
- Silicon nitride: $229 \text{ (MJ/ tube)} \times 1 \text{ (tubes)} = 229 \text{ MJ}$

Looking over the entire process, the exergy inputs for steel and silicon nitride were 130999 GJ and 130637 GJ respectively, while exergy outputs were 5417 GJ and 5055 GJ. Using silicon nitride reduced 362 GJ of input and output exergy compared to steel.

From the above results, it was shown that although one silicon nitride tube required 7 times more exergy in manufacturing process, frequency of replacement decreased due to its high conservative property, which allowed furnace with highly efficient structure that reduced electricity consumption, and therefore, exergy consumption level was smaller compared to steel in total throughout the lifecycle of manufacture, use, and disposal.

3.5 Rationalization consideration

Assuming current system, we proposed guideline for rationalization for using ceramics or steel. Then we summarized the current state and direction of rationalization of casting system.

3.5.1 Steel member

Highly economical steel member is mainstream of heater tube. When use of steel member is assumed, development of material or coating technology to prevent corrosion by molten aluminum is necessary to increase lifespan. Also, steel has excellent recyclability, and it is important to increase recycling efficiency.

3.5.2 Ceramics member

To promote rationalization of ceramics manufacture, as mentioned above, increased efficiency of granulation and sintering operations that have particularly high consumption among all operations is mandatory. This improvement is highly significant to reduce environmental impact and to counter steel members that are highly economical.

① Granulation

While metal process such as in steel involves melting raw material at high temperature and mixing and reaction by dispersal ability of liquid medium, ceramics use solid powder without dispersal ability in gravitational field. Therefore, it is a process with inherent inefficiency, where water and binder that do not remain in the final product are added between solid particles for mixing, and energy is required to remove them.

When water is introduced, distance between particles can be reduced and mixing becomes easy, but large amount of latent heat must be consumed to evaporate the water in the slurry in the post-operation dry granulation. The input energy is transferred to water as heat, evaporates, and released outside the system along with entropy as steam. Therefore, to reduce

exergy consumption during granulation, although reduction of water including selection of deflocculant and adjustment of granularity are necessary, the time required for mixing in preliminary operation will increase. To reduce exergy consumption in the granulation operation, optimization of water content while considering effect on preliminary and following operations is necessary.

LPG is used as fuel in granulation. When LPG is used, input exergy will produce water and carbon dioxide unavoidably during combustion, other than in drying of slurry and granulation, and exergy is consumed for releasing them from the system. If electricity is used instead of LPG, input exergy may seem to be reduced. In this case, exergy consumption in plant may be reduced, but exergy is actually consumed outside (at a power plant). This time, LPG was used in the granulation operation since cost was prioritized.

② Sintering

Figure 11 is a conceptual diagram that summarizes the relationships of material, product, and input exergy for rationalization. It is assumed that reference material (exergy = 0) and material have chemical exergy and exergy derived from surface energy, and material and product (sintered body) have difference in exergies derived from surface and interface, as well as arrangement.

Stable material with highly covalent silicon nitride requires large amount of exergy in running the furnace and heating the refractory materials, in addition to exergy equivalent to the barrier of activation energy. These unavoidably become waste exergy, and waste heat recovery must be considered.

To reduce exergy consumption, input and output can be lessened by using low exergy material and by utilizing the energy of the material. Chemical exergy of silicon nitride is high at 1877 kJ/mol. Moreover silicon nitride particles undergo separate operations for nitrification of silicon and sintering of silicon nitride obtained, and each operation produces waste heat.

On the other hand, chemical exergy of silicon is calculated to be 851 kJ/mol, or about half of silicon nitride. To reduce exergy consumption, it is effective to shift from silicon nitride powder to silicon, powder and to conduct nitriding and sintering in one operation. Although this process is known as post sintering involving reaction-bonding, it is not widely done because control of heating in nitrification process is difficult and mixing using water medium is difficult since silicon itself is active. In the future, to make the process practical, it is necessary to develop a catalyst that allows mixing with water medium in short time and allows nitrification at low temperature using rough silicon particles. Also, to increase efficiency, one way is to increase sintering temperature by increasing size of drying and sintering

furnaces that will increase production volume per unit time, but optimization of total system must be conducted while considering facilities investment and production volume.

Exergy, which was born from heat engineering, is considered as common thread between effective energy and materials, but it is not sufficiently systematized from physical perspective such as dealing with interface and surface as mentioned above. This is future issue in increasing the accuracy of the index.

③ Design and others

As mentioned earlier, since ceramics is extremely stable in molten aluminum, it does not have to be solid body. Not only does hollow structure design and process reduce amount of material used, but also will decrease heat stress by thinning and will shorten sintering time, and these are extremely useful for improving efficiency.

On the other hand, ceramics is not suitable for recycling. Both company and consumer must become conscious of using ceramics members as long as possible because they were manufactured using great amount of exergy input. In technological development, considering the characteristics of ceramics, development of design and process that allows exchange of damaged parts and reparable structure is necessary.

3.5.3 Innovation in casting system

Looking at the overall casting operation, there are two operations in which solid is melted, and heat is radiated

considerably in delivery process (Figure 4). Exergy necessary to melt solid was calculated to be about 19000 GJ (4300 per ton). To decrease this, development of molten metal delivery system, where molten aluminum melted outside is placed in insulating container, delivered directly into plant in molten state, temperature adjusted in holding furnace, and then formed, is being done by major automobile companies. It is expected that efficiency will increase since one process of melting-solidification is reduced. However, currently there are problems such as insufficient insulation of the transporting container that demands external heater during delivery process, as well as high fuel consumption in transportation process because the container itself is heavy. Delivery of molten metal is highly efficient system in principle and diffusion is expected, but development of lightweight container with excellent insulation is the key.

The centralized melting furnace, which will become the center of the above delivery system, will be on continuous run once aluminum is melted in the furnace to maintain the molten state. Considering that it is necessary to put in energy regardless of amount, the ultimate system will be to deliver the metal into the plant as solid, and to melt only necessary amount to produce the product. There are several issues before this system can be realized, such as heating source that enables instant melting, excellent insulation which is component of system, large ceramic tube and container that the molten metal will not adhere, engine design that allows easy disassembly, and establishment of recovery system of disposed engine in the society. It is necessary to solve individual issues while considering the overall exergy balance.

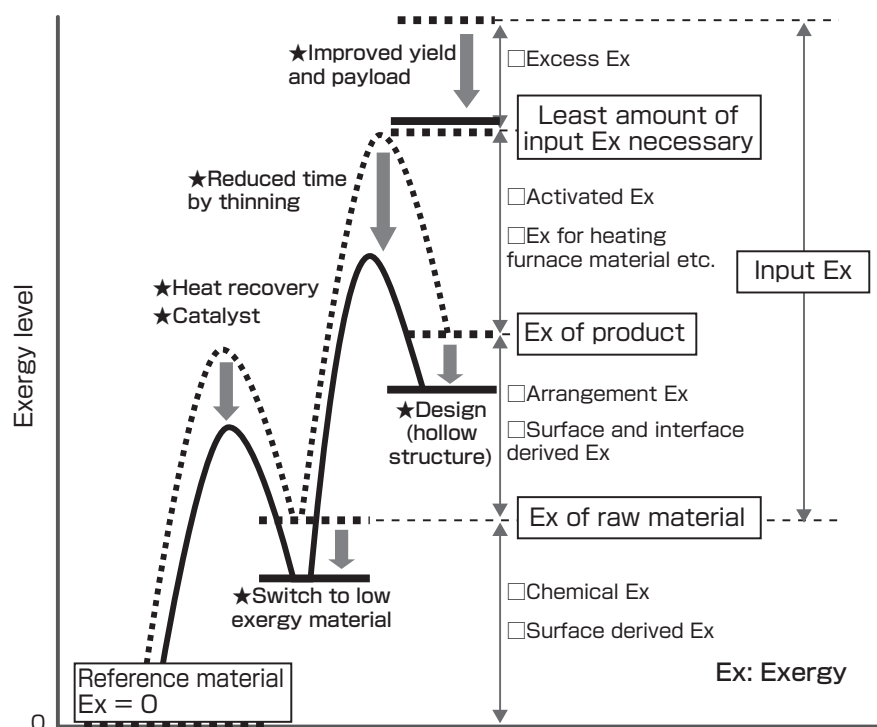


Fig. 11 Rationalization of ceramics process.

4 Summary

4.1 Evaluation of manufacture

Exergy analysis was done in case where members were manufactured with ceramics and steel, used as production member for 7 years in casting line for aluminum engine, and then disposed.

- ① Exergy input per product was 4175 MJ for ceramics and 621 MJ for steel, and significantly higher exergy was consumed for ceramics compared to steel.
- ② Exergy fixed in ceramics was 229 MJ, or 5.5 % of exergy input, and most are emitted outside the system.
- ③ By operation, granulation and sintering consumed 80 % of total input.
- ④ As result of high exergy input, ceramics have high conservation. When it is used in molten aluminum using this characteristic and used for 7 years, exergy consumption is reduced 362 GJ compared to steel.

4.2 Rationalization consideration

Assuming current system, guidelines for rationalization when ceramics or steel members were used and technologies needed for rationalization of casting system as a whole were summarized.

① Steel

- Development of material and coating technology that is not readily corroded by molten aluminum.

② Ceramics

To improve manufacturing efficiency of ceramics, rationalization of granulation and sintering operations that have significantly high consumption is mandatory.

- Optimization of water content while considering effect on preliminary and following operations, such as selection of deflocculant and adjustment of granularity.
- Catalyst that allows nitrification at low temperature using rough silicon particle, or combination of nitrification and sintering processes.
- Hollow structure design. Reduced amount of raw material and shortened sintering time.
- Technological development for exchange and repair of parts to use ceramics member manufactured with large exergy input.

③ Casting system

- To increase efficiency of delivery system of molten metal, development of transportation container that is lightweight and has excellent insulation is the key.
- System for delivering the metal as solid and melting only necessary amount to be used for product. Several issues must be solved including heating source that allows instant melting, large ceramics tube and container with high insulation and without adhesion of molten metal, engine

design with higher disassembly, and diffusion of recovery system of waste engine in the society.

5 Future prospect

Based on above considerations, we summarized the efficacy and issues of exergy analysis.

5.1 Efficacy of exergy analysis

① Normally, environmental impact assessment is conducted at manufacture phase and the content is already determined in the general plan, so options as measures for impact reduction are limited. It is necessary to forecast resource consumption and environmental impact of systems across wide-ranging level such as planning, R&D, and design, and the result should be fed back to technology and manufacturing. Exergy that links matter and energy is index appropriate for preliminary evaluation due to its characteristic, and effective use is desired.

② Cycling system is the outer shell of sustainability. To reduce input of resource and energy from outside needed to drive the cycling system, rationalization of system using exergy must be done swiftly.

③ Although case of ceramics and metal was discussed in this paper, exergy is not limited to certain field or subject. Final goal is to link manufacturing (micro factor) to global level sustainability (macro result). It is possible, in principle, to calculate consumption speed of exergy using macro input and output data at national level for emission. This may become index for shift to sustainability.

5.2 Issues that must be improved

① Powder particle and sintered body made from that material were evaluated using same chemical exergy. In the future, it is necessary to have index that shows difference in condition such as surface and interface energy.

② Exergy is not appropriate for evaluating rarity or hazard, and it is necessary to conduct multifaceted evaluation by combining with other indices.

Acknowledgements

This paper was written with hints from some discussions that arose within the Minimal Manufacturing Working Group composed of cross-disciplinary members of AIST, and we are grateful to people in the Working Group.

Terminology

Term 1. Exergy: Effective energy that can be converted to other energy.

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Discussion with Reviewers

1 Importance of linkage between technology and index

Question & comment (Norimitsu Murayama)

Figure 2 shows the importance of evaluation index in synthesiological approach to research, and it is the heart of message of this paper. Between technological development and new evaluation index, what is made in “manufacture”? Also, isn’t the arrow from index to technological development “measure”? On contrary, isn’t the arrow from new evaluation index to technological development “advancement”?

Answer (Hideki Kita)

The object “manufactured” is product or process obtained in the process of technological development. Evaluation index and technological development are joined with double-headed arrow to indicate that improvement and progress take place by mutually reflecting their results. Index becomes “advanced” and the technological development improves in “competitiveness” as result of action of turning the cycle of “concept,” “development,” and “evaluation,” and these were placed outside the triangle.

2 Manufacturing efficiency

Question & comment (Norimitsu Murayama)

Assuming, for example, a sintering process with 100 % alumina, exergy is zero because alumina is a reference material and the exergy fixed in the sintered compact is zero. Therefore, even if there the total exergy input is varied, “manufacturing efficiency” will always be zero, and the differences in process will not be expressed. Rather than using the expression “manufacturing efficiency,” I think it is more appropriate to use the term, for example, “fix ratio of exergy in components.” Also, I think overall performance of the manufacture process can be expressed accurately by showing the values of both “fix ratio of exergy in components” and total exergy input.

Answer (Hideki Kita)

Exergy is a concept that originated in thermodynamics and applied to matter. In applying exergy to matter, as exemplified by the point that exergies for powder and ingot that have different bonding condition are same, as far as I can understand, systematization is insufficient from physical perspective in addressing surface and interface energy. It is one issue as a manufacturing index, and I mentioned this point in Section 5 of the text.

3 Performance evaluation of manufacture process taking in consideration the durability of components

Question & comment (Norimitsu Murayama)

Total exergy input indicates how distant it is from stable condition in nature, and it can be considered scientific expression of cost. The paper discusses the durability of ceramics components, but wouldn't the value of total exergy input/durable years be index that expresses the performance of entire manufacture process?

Answer (Hideki Kita)

I think the value of total exergy input/durable years is one of indices that express performance. On the other hand, considering environmental load, durable year (durability) itself is important guide. For example if the values of total exergy input/durable years are same, disposed amount of product with longer durability become less.

4 Future direction of evaluation method using exergy

Question & comment (Koichi Mizuno)

Based on the present comparison between the two kinds of heater tubes made from ceramics and iron (steel??), do you consider future research directions?

There are two ways. One is to widen out to operations other than heater tube (horizontal spread), on which the Reviewer do not have advice.

Another is deeper consideration of heater tube (vertical

consideration). For example, to increase exergy efficiency further, technology to increase efficiency by recycling iron, or iron alloy technology to prevent dissolving in molten aluminum can be considered. Additionally, in ceramics, energy conservation may be considered in granulation and sintering operations that consume large energy in the manufacture process. For latter, "soft solution process" has been developed for manufacturing ceramics to avoid high-temperature sintering.

Answer (Hideki Kita)

Considering your comment, in Section 3.5, we showed guideline for rationalization of cases where ceramics or iron members were used, assuming current system, and then we summarized the current status and the direction of rationalization of casting system. 5 Future prospect is a mere summary.

For direction, we added guideline of rationalization of iron and ceramics in Section 3.5. Particularly for ceramics, we described the technological prospects for further energy conservation of granulation and sintering processes that consumes high amount of energy in the manufacturing process, along with Figure 11. Although soft solution process is an effective method for small, lightweight members or thin film, it is not process appropriate for large silicon nitride sintering compact addressed in this paper. Therefore we did not include it in our consideration.

Launch of AIST journal *Synthesiology*

— Discussion with Japanese researchers at the University of Illinois at Urbana-Champaign —

Hitoshi Ohsaki* and Yuji Sato**

[Translation from *Synthesiology*, Vol.1, No.3, p.222-228 (2008)]

This paper presents the discussion with Japanese researchers of computer science at the University of Illinois concerning the launch of journal *Synthesiology* and the underlying philosophy of AIST. Based on questions and comments that were raised in the discussion, we indicate current problems and issues that must be considered in the future for the journal.

1 Background

This article is a commentary based on the discussion between the authors and the Japanese researchers at the University of Illinois at Urbana-Champaign (UIUC), concerning the journal *Synthesiology* launched in January 2008 by the National Institute of Advanced Industrial Science and Technology (AIST).

First, we briefly describe the background of how this article came to be. Ohsaki, one of the authors, was conducting the research on system verification and tree automata at UIUC for one year starting June 2007 in the AIST overseas research program. His research activities at UIUC include giving lectures to graduate students to explain his research, and managing seminars for Japanese researchers in the computer science field (CS Seminar).

The CS Seminar started in August 2007 as a place for exchange among UIUC Japanese researchers. The objective of the seminar was to introduce stances of individual researchers of different disciplines. The seminar participants could make comments or ask questions based on their own experience and knowledge. The seminar also provided a forum for free discussion after presentation by the topic provider.

The backgrounds of participants became apparent as more seminars were held. Even in same computer science field, research styles and involvement with society through research differed greatly. Positions as university faculty, graduate student, or researcher seemed to influence the ways of thinking of individuals.

Using the opportunity provided by the CS Seminar, on March

2008, Ohsaki served as a topic provider to introduce the new journal and the underlying principle of AIST, followed by discussion by seminar participants. We had absolutely no clue to whether AIST's new challenge would be treated as mere self-gratification or whether people outside may have clearer view of the course of AIST than the people inside the organization.

The *Synthesiology* Editorial Committee had initially suggested us a roundtable talk. However, we did not employ the committee's proposal because we did not want to interfere with the free discussion atmosphere and we wanted to make our statement.

Therefore, the text is mainly speculation by the authors while citing comments of researchers who participated in free discussion at the seminar.

2 Academic research and fieldwork

Full Research, which is goal of AIST, is composed of three types of researches: *Type 1 Basic Research*, *Type 2 Basic Research*, and *Product Realization Research*. We explain the terminologies and basic concepts according to the article on *Full Research*^[1].

Type 1 Basic Research is defined as “research to create new knowledge that is not in conflict with the discipline of knowledge based on the specific knowledge of the closed discipline.” This research attempts to gain new knowledge that is independent and does not mutually interfere with existing knowledge, to organize new knowledge, and to contribute to the overall knowledge system. In general, it is known as “academic research.”

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Type 2 Basic Research is defined as “research to create something that is socially perceivable by fusing knowledge not limited to certain discipline and by creating new knowledge as needed.” The research process is unique since there is no limit set on discipline. It is known to produce less visible results in form of papers even if it is equally hard work as conventional research, because research process itself is not considered to be research result according to conventional academic standard. It is also characterized by various research risks such as requiring long time before tangible results can be obtained, and is often wrought with extensive problems that must be solved before further research can be continued.

However, activities that pursue result wanted by the society using specialized skills and knowledge create opportunity where basic research and society can recognize each other. At the Research Center for Verification and Semantics where Ohsaki is currently affiliated with, research in which society is observed and framework for explaining it is created is called “fieldwork”^[2]. This style of research can be an instance of *Type 2 Basic Research* according to the definition as described above.

On the other hand, it is difficult to immediately understand the concept of the two basic researches that is not yet widely accepted, only by written description. Therefore, schematic diagram shown in Figure 1 was used to explain *Type 1* and *Type 2 Basic Researches* in the CS Seminar.

Two basic researches were represented by two ovals on left and right. Mutual interaction of the two basic researches was explained as large arrows going from one to the other. The flows from *Type 1* to *Type 2 Basic Research* were explained by large arrows that connected the ovals. Also, to explain the characteristics of two basic researches, we explained that *Type 1 Basic Research* was composed of self-contained circular motion, while *Type 2 Basic Research* was composed of motion that flowed across all disciplines.

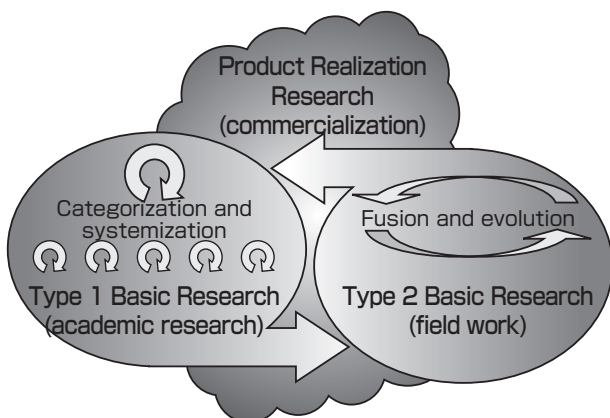


Fig.1 Two types of basic research.

Both *Type 1* and *Type 2 Basic Researches* can move on to *Product Realization Research*. Unlike the conceptual diagram in “Research Methodology to Realize Innovation”^[3], we added a cloud representing *Product Realization Research* between the two basic researches. The Figure shows that *Product Realization Research* results from constant exchange between the two basic researches.

Some young researchers in the CS Seminar commented, “It seems difficult to conceive the image of shuttling between the two basic researches” (Daimon, one of the CS seminar participants), but there were no particular objections or questions to this explanation.

3 “*Type 2 Basic Research* = Practical Application Research” ?

In order to progress from results obtained in basic research to commercialization phase, it is necessary that all people who so wish can readily use the research result. This is flow from basic research phase to practical application research phase, and then to commercialization. On the other hand, as mentioned in the previous section as issue for *Type 2 Basic Research*, there is no guarantee that the basic research result will develop into successful business. Figure 2 shows the flow from basic research to commercialization and the problems often encountered.

For presentation up to this point, the following questions were raised by the CS Seminar participants. Honorifics of the participants are abbreviated.

[Minami] Then, is *Type 2 Basic Research* same thing as practical application research?

Practical application research shown in Figure 2 is one of the research phases that lead to future commercialization. It is an attempt to obtain research result in form recognizable to the society. Therefore, according to definition in the previous section, “*Type 2 Basic Research* \supseteq practical application research (if practical application research, then *Type 2 Basic Research*)” is justified. On the other hand, if “*Type 2 Basic Research* \subseteq practical application research (if *Type 2 Basic Research*, then practical application research)” is true, according to the diagram “Basic Research \rightarrow Practical Application Research \rightarrow Commercialization,” the objective of *Type 2 Basic Research* is commercialization. However, in *Type 2 Basic Research*, researcher may wish to extract elemental technologies and investigate specific material, observe them with scientific eyes, and systematize this technique. The objective of *Type 2 Basic Research* may not necessarily be commercialization. Therefore, it is more natural to think “*Type 2 Basic Research* $\not\supseteq$ practical application research.”

Synthesiology claims itself to be journal for presenting

the result of *Type 2 Basic Research*^[1]. Certainly, research processes, which are rarely considered as topics of paper in conventional practice, are important in *Type 2 Basic Research*. *Synthesiology* looks at the research processes and views them as paper topics.

Combined with discussion “*Type 2 Basic Research* \supseteq practical application research,” we think it is correct to say *Synthesiology* is a journal for presenting the result of *Type 2 Basic Research*, particularly of practical application research (as described in Figure 2) and its research process.

Next, following comments were made about Figure 2.

[Sato] In some case of companies and projects, the exit of research is very clear, so the arrows may point the opposite direction. For example, when the image of the product is presented as development target (by request of business division), research is most often started by considering which basic research results are needed to fulfill the request and what kind of people will be assigned to the project.

For some companies that work steadily on product development or for those that try to get specific result in short-term research project, perhaps things will be accomplished by top-down management. However in *Type 1 Basic Research*, research is motivated by desire to “discover the unknown.” Therefore, it is rare that newly found knowledge leads directly to commercialization. Particularly in research of basic science, it often requires long time before the result is put to use in the society or it may even get lost. Figure 2 describes the situations encountered by the researcher before the result of basic research reaches the commercialization phase.

In product development where the image at the exit is very clear, if one aspires to develop an extremely ambitious product, the result of basic research result needed to realize the product cannot be found easily. Therefore, to obtain totally new basic research result and to take the basic research result obtained to commercialization, the research is conducted along the flow shown in Figure 2. In this case, one can easily imagine researchers falling into the situations described in Figure 2.

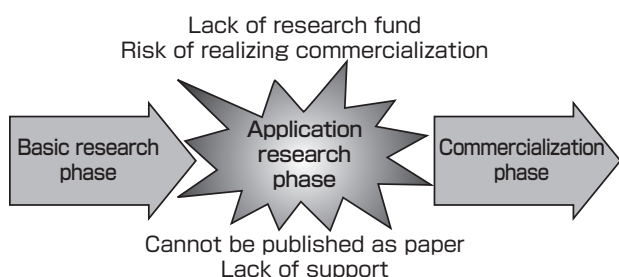


Fig.2 Research in practical application phase.

4 Behind-the-scene stories and technical reports

In the introduction of the launch of new journal, there is following passage: “...These technology integration research activities have been kept as personal know-how, however. They have not formalized in universal knowledge.” Comments were raised that this claim may cause misunderstandings.

[Sato] The new journal says that it will publish research process of *Type 2 Basic Research*, but it is already established practice in companies to write up process leading to commercialization and behind-the-scene stories of the project. Such articles are published as technical reports or company reports. The reports of other companies of same industry can be viewed in the company library. They are also available to general public.

For example, Hitachi Groups publishes the Hitachi Hyoron (<http://www.hitachihyoron.com/>) regularly to introduce new products and systems and to report the direction of business and technology. The title for February 2008 issue was “Special: Latest Technological Development in Electric and Energy Field”^[4]. Unlike papers written by researchers of universities and research institutes, they contain descriptions of technologies and applications related to the new product, and stories during the development process, along with introduction of new products and system such as “Work on globalization of nuclear energy business” and “Features and application of Hitachi H-25 Gas Turbine.”

Also, *Mitsubishi Electric Technical Report*^[5], *NEC Technical Report*^[6], and *Toshiba Review*^[7] are distributed free on the Internet, and can be viewed by anyone. *NTT DoCoMo Technical Journal*^[8] and *Toyota Technical Review*^[9] are sold as magazines.

Company and technical reports introduce and explain the activities within the organization, and in most cases do not accept submission from outside. Also articles that depart from philosophy and goal of particular corporation are not likely to be published. Also, some research fields have culture of not wanting to include knowledge of “what ought to be” and synthetic judgment. In this situation, even if the researchers who are grounded in basic research make some synthetic judgment to make the result useful to the society, there are few receptacles that allow systematic discussion of such thinking.

5 Undisclosed research result

[Furukawa] In *Type 2 Basic Research*, I think there are many cases where case-studies become research result, but aren't there also many cases that cannot be disclosed due to non-disclosure agreements?

In companies, in principle, research results that link directly to profit are non-disclosed. For example, research on technology to increase yield of LSI is a major topic in the semiconductor industry. In general, yield is ratio of volume of raw material to volume of product. In the semiconductor industry, yield is the ratio of good products that show certain performance in all products produced such as IC chips and memories. Normally, yield is set at certain percentage to determine the product price. That means if the yield improves above certain percentage, the difference becomes company profit.

Therefore, the details of yield improvement technology for LSI are extremely sensitive information for semiconductor companies. Even if the researcher or technician at a company proposes idea to improve yield, it is general practice not to disclose that information outside the company including academic societies.

On the other hand, in principle, universities and public research institutes attempts to advance science and technology by using and diffusing accumulated knowledge. In reality, there are many cases where research results are intentionally not disclosed. If the research result is expected to cause economic loss, disclosure may be slowed or not done at all, to provide time to take measures against major loss. Also, in research whose objective is commercialization, results may not be disclosed due to strategic reasons. How were the results obtained? Are the results reproducible? Not disclosing the heart of research prevents the competitors who are also working on similar products from catching up.

There is choice of disclosing the research result as patent. It is choice when there is financial security to start the next phase of research after some progress in application research. However, since the screening period for patent may require two to three years, another choice is licensing where exclusive rights to use the research result is provided. In this case, the agreement is not to disclose the details at least during the agreement period. As result, since not much can be written up as paper, outsiders make evaluation like “the research was done but not much result was obtained.”

Negotiations and agreements on how much can be published as academic paper are settled prior to starting research. Here, the research leader’s ability to negotiate wisely with future development in mind greatly influences how much can be written in the paper. The “Japanese-style valley of death of research” where excellent research results fail to become innovations is said to be result of poor leadership. The result that can be disclosed differ greatly depending on the leader.

In *Type 2 Basic Research*, particularly those that aim at commercialization and product realization, we can see that the results may not be disclosed for various reasons. However, *Synthesiology* was not created as refuge for

researchers who do not have a place to make their statements. The objectives of this journal are to record matters that researchers feel that other researchers should know, and to reconstruct and use accumulated knowledge.

6 Expectations and doubts for *Synthesiology*

There were many comments on expectations for future activities of *Synthesiology* as journal to publish results of application research and its research process. On the other hand, there were comments that contrary to the wish of the journal to publish good papers, good papers may seek publication in traditional academic journals.

[Sato] From the standpoint of someone (outside of AIST) wanting to submit papers, higher the quality of the paper, it is natural that they wish to submit papers to renowned, traditional academic journals. Papers for commercialization and product development are also accepted if they are innovative businesswise or superior as product, so may not be necessarily the priority to submit the papers.

This problem is common to all newly launched journals. *Synthesiology* tries to extract certain laws and general theory for “synthesis” from a posteriori knowledge. Therefore, by targeting researchers who wish to have their papers evaluated from the perspective from synthetic learning, compartmentalization with traditional academic journals is possible. Also, *Synthesiology* has role to transmit messages to researchers who wish to establish *Type 2 Basic Research* as a discipline.

On the other hand, as indicated in Section 4, many companies that do research, development, and product realization publish article on application research results and R&D process in their company publications and disclose them to the public. *Synthesiology*, as a new project for AIST, also tries to publish articles on application research results and R&D process. Therefore, one will be unable to see difference with corporate technical reports if only this point is emphasized.

Papers that discuss research processes of basic research way before product realization is basically different from articles of corporate technical reports. Even if majority of the papers published in *Synthesiology* are submitted from within AIST, it will be strike a chord in people outside AIST if they describe what kind of thought process researchers have when they are sandwiched between academia and society, and how they sublimate their research.

Whatever it is, we must look at the future of the *Synthesiology* to draw conclusions about success or failure of the new journal.

On the other hand, it can be said that any research is worthy

of publication if the results and research processes contain universal statement.

[Inaba] I think the uniqueness and value of *Synthesiology* can be claimed as open opportunity to publish behind-the-scene stories of research, without limiting the topic to results and research processes of application research. In that sense, AIST, which is the largest Japanese research institute for basic research, must have lots of researchers that can provide stories.

Can the famous “First Draft of a Report on the EDVAC”^[10] written by John von Neumann at the dawn of computers be called paper of *Type 2 Basic Research* or a paper that described “ought” knowledge. At the time, computer technology was concealed as classified information. Particularly, there were only few papers that described the details of ENIAC, the predecessor of EDVAC^[11]. The “First Draft” was more like an academic paper that comprehensively explained the architecture of stored-program computer (the archetype of current computer) from mathematician’s perspective, rather than a technological document describing the state-of-art technology of the time. In fact, it was conceptual, though universal, explanation of basic components of stored-program computer and flow of arithmetic processing. Influenced by this “First Draft” and several papers by von Neumann that followed, stored-program computers were developed around the world after 1948, and diffused globally as standard of computers^[12].

The example of von Neumann paper is perhaps a special case. However, following lessons can be learned from this example. In academic insight gained by studying, analyzing, and synthesizing the result of *Type 2 Basic Research*, boundary between ought knowledge (“value”) and factual knowledge (“fact”) is unclear. Indeed, even if the paper is composed only from factual knowledge, subjective statement of the author seeps out between the lines.

What then is a paper for ought knowledge? Traditional “scientific” paper is a paper formed of factual knowledge and thus conclusion is drawn from accumulation of facts. The conclusion, on the other hand, can be convinced within particular discipline of knowledge.

However, ought knowledge include subjective statements. Aside from apparent mistake, paper with stance of “no ought from an is” demands final judgment by the readers for appropriateness or even truthfulness of the statement.

On the other hand, if the stance that ought knowledge and factual knowledge are indivisible^[13], the paper of ought knowledge is an opportunity to state conclusion drawn by accumulation of facts within the framework including social norms or values. There is possibility that truthfulness or appropriateness may become difficult to judge.

Regardless of the stance one takes in paper that discusses ought knowledge and subjective statement, the situation shunned by most academic journals is accepted, and ought knowledge papers now has opportunity for publication. *Synthesiology* states that it will accept this difficult situation as a journal to achieve its initial objectives. I think this stance makes this journal unique.

The problem of review process was indicated concerning the point that there were papers from multiple research fields.

[Sato] Submitted papers include those of diverse products and fields. Therefore, how do you maintain evenness of review quality, and how do you maintain fairness of review processes and results?

Discussion between reviewers and authors are published at end of each paper, to keep the review process transparent. Whether the quality of review is maintained or not can be checked by reading the discussion. Errors that can be verified objectively can be corrected in the review process, while the following points can be communicated: (1) how reviewers see truthfulness or appropriateness of statements (conclusions) that include subjective elements, and (2) that the final judgment is left to the readers.

For a new journal to ask submission of papers under its unique objective may seem arrogant from outside. However, if there are more people outside AIST who agree with the objective and attempt to increase the significance of the journal, the journal as well as the underlying philosophy of AIST will be justified.

[Minami] For that purpose, is raising awareness of the journal a priority, or is it to have people understand the objective of new journal launch?

There is no conclusion in the discussion of “chicken or egg.” Rather than discussing the journal, perhaps the priority should be how to establish the unique concept of AIST where research is categorized into *Type 1 Basic Research*, *Type 2 Basic Research*, and *Product Realization Research* rather than basic research, application, research, and design development.

7 Summary

In the discussion at the CS Seminar, we had an opportunity to review the ideological objective of the journals, as exemplified by the launch of *Synthesiology*. Also, several issues that must be considered in the present and reviewed in the future were raised. They are not easy at all to solve. However, how these issues are resolved will be the key to success of new journal *Synthesiology*.

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Editorial Policy

Synthesiology Editorial Board

Objective of the journal

The objective of *Synthesiology* is to publish papers that address the integration of scientific knowledge or how to combine individual elemental technologies and scientific findings to enable the utilization in society of research and development efforts. The authors of the papers are researchers and engineers, and the papers are documents that describe, using “scientific words”, the process and the product of research which tries to introduce the results of research to society. In conventional academic journals, papers describe scientific findings and technological results as facts (i.e. factual knowledge), but in *Synthesiology*, papers are the description of “the knowledge of what ought to be done” to make use of the findings and results for society. Our aim is to establish methodology for utilizing scientific research result and to seek general principles for this activity by accumulating this knowledge in a journal form. Also, we hope that the readers of *Synthesiology* will obtain ways and directions to transfer their research results to society.

Content of paper

The content of the research paper should be the description of the result and the process of research and development aimed to be delivered to society. The paper should state the goal of research, and what values the goal will create for society (Items 1 and 2, described in the Table). Then, the process (the scenario) of how to select the elemental technologies, necessary to achieve the goal, how to integrate them, should be described. There should also be a description of what new elemental technologies are required to solve a certain social issue, and how these technologies are selected and integrated (Item 3). We expect that the contents will reveal specific knowledge only available to researchers actually involved in the research. That is, rather than describing the combination of elemental technologies as consequences, the description should include the reasons why the elemental technologies are selected, and the reasons why new methods are introduced (Item 4). For example, the reasons may be: because the manufacturing method in the laboratory was insufficient for industrial application; applicability was not broad enough to stimulate sufficient user demand rather than improved accuracy; or because there are limits due to current regulations. The academic details of the individual elemental technology should be provided by citing published papers, and only the important points can be described. There should be description of how these elemental technologies

are related to each other, what are the problems that must be resolved in the integration process, and how they are solved (Item 5). Finally, there should be descriptions of how closely the goals are achieved by the products and the results obtained in research and development, and what subjects are left to be accomplished in the future (Item 6).

Subject of research and development

Since the journal aims to seek methodology for utilizing the products of research and development, there are no limitations on the field of research and development. Rather, the aim is to discover general principles regardless of field, by gathering papers on wide-ranging fields of science and technology. Therefore, it is necessary for authors to offer description that can be understood by researchers who are not specialists, but the content should be of sufficient quality that is acceptable to fellow researchers.

Research and development are not limited to those areas for which the products have already been introduced into society, but research and development conducted for the purpose of future delivery to society should also be included.

For innovations that have been introduced to society, commercial success is not a requirement. Notwithstanding there should be descriptions of the process of how the technologies are integrated taking into account the introduction to society, rather than describing merely the practical realization process.

Peer review

There shall be a peer review process for *Synthesiology*, as in other conventional academic journals. However, peer review process of *Synthesiology* is different from other journals. While conventional academic journals emphasize evidential matters such as correctness of proof or the reproducibility of results, this journal emphasizes the rationality of integration of elemental technologies, the clarity of criteria for selecting elemental technologies, and overall efficacy and adequacy (peer review criteria is described in the Table).

In general, the quality of papers published in academic journals is determined by a peer review process. The peer review of this journal evaluates whether the process and rationale necessary for introducing the product of research and development to society are described sufficiently well.

In other words, the role of the peer reviewers is to see whether the facts necessary to be known to understand the process of introducing the research finding to society are written out; peer reviewers will judge the adequacy of the description of what readers want to know as reader representatives.

In ordinary academic journals, peer reviewers are anonymous for reasons of fairness and the process is kept secret. That is because fairness is considered important in maintaining the quality in established academic journals that describe factual knowledge. On the other hand, the format, content, manner of text, and criteria have not been established for papers that describe the knowledge of “what ought to be done.” Therefore, the peer review process for this journal will not be kept secret but will be open. Important discussions pertaining to the content of a paper, may arise in the process of exchanges with the peer reviewers and they will also be published. Moreover, the vision or desires of the author that cannot be included in the main text will be presented in the exchanges. The quality of the journal will be guaranteed by making the peer review process transparent and by disclosing the review process that leads to publication.

Disclosure of the peer review process is expected to indicate what points authors should focus upon when they contribute to this journal. The names of peer reviewers will be published since the papers are completed by the joint effort of the authors and reviewers in the establishment of the new paper format for *Synthesiology*.

References

As mentioned before, the description of individual elemental technology should be presented as citation of papers published in other academic journals. Also, for elemental technologies that are comprehensively combined, papers that describe advantages and disadvantages of each elemental technology can be used as references. After many papers are accumulated through this journal, authors are recommended to cite papers published in this journal that present similar procedure about the selection of elemental technologies and the introduction to society. This will contribute in establishing a general principle of methodology.

Types of articles published

Synthesiology should be composed of general overviews such as opening statements, research papers, and editorials. The Editorial Board, in principle, should commission overviews. Research papers are description of content and the process of research and development conducted by the researchers themselves, and will be published after the peer review process is complete. Editorials are expository articles for science and technology that aim to increase utilization by society, and can be any content that will be useful to readers of *Synthesiology*. Overviews and editorials will be examined by the Editorial Board as to whether their content is suitable for the journal. Entries of research papers and editorials are accepted from Japan and overseas. Manuscripts may be written in Japanese or English.

Required items and peer review criteria (January 2008)

	Item	Requirement	Peer Review Criteria
1	Research goal	Describe research goal (“product” or researcher's vision).	Research goal is described clearly.
2	Relationship of research goal and the society	Describe relationship of research goal and the society, or its value for the society.	Relationship of research goal and the society is rationally described.
3	Scenario	Describe the scenario or hypothesis to achieve research goal with “scientific words” .	Scenario or hypothesis is rationally described.
4	Selection of elemental technology(ies)	Describe the elemental technology(ies) selected to achieve the research goal. Also describe why the particular elemental technology(ies) was/were selected.	Elemental technology(ies) is/are clearly described. Reason for selecting the elemental technology(ies) is rationally described.
5	Relationship and integration of elemental technologies	Describe how the selected elemental technologies are related to each other, and how the research goal was achieved by composing and integrating the elements, with “scientific words” .	Mutual relationship and integration of elemental technologies are rationally described with “scientific words” .
6	Evaluation of result and future development	Provide self-evaluation on the degree of achievement of research goal. Indicate future research development based on the presented research.	Degree of achievement of research goal and future research direction are objectively and rationally described.
7	Originality	Do not describe the same content published previously in other research papers.	There is no description of the same content published in other research papers.

Instructions for Authors

Synthesiology Editorial Board
Established December 26, 2007
Revised June 18, 2008

1 Types of contributions

Research papers or editorials should be submitted to the Editorial Board.

2 Qualification of contributors

There are no limitations regarding author affiliation or discipline as long as the content of the submitted article meets the editorial policy of *Synthesiology*, however, authorship should be clearly stated. (It should be clearly stated that all authors have made essential contributions to the paper.)

3 Manuscripts

3.1 General

1) Articles may be submitted in Japanese or English. Accepted articles will be published in *Synthesiology* (ISSN 1882-6229) in the language they were submitted in. All articles will also be published *Synthesiology* - English edition (ISSN 1883-0978). The English edition will be distributed throughout the world approximately four months after the original *Synthesiology* issue is published. Articles written in English will be published in English in both the original *Synthesiology* as well as the English edition. Authors who write articles for *Synthesiology* in Japanese will be asked to provide English translations for the English edition of the journal.

2) The manuscript shall be prepared using a word processors or similar devices, and printed on A4-size portrait (vertical) sheets of paper. The category of article (research paper or editorial) shall be stated clearly on the cover sheet.

3.2 Structure

1) The manuscript should include a title (including subtitle), abstract, the name(s) of author(s), institution/contact, main text, and keywords (about 5 words).

2) Title, abstract, name of author(s), and institution/contact shall be provided.

3) The length of the manuscript shall be, about 6 printed pages including figures, tables, and photographs.

4) The title should be about 10-20 Japanese characters (5-10 English words), and readily understandable for a diverse readership background. Research papers shall have subtitles of about 15-25 Japanese characters (7-15 English words) to

help recognition by specialists.

5) The abstract should be about 200 Japanese characters (75 English words).

6) The main text should be about 9,000 Japanese characters (3,400 English words).

7) The article submitted should be accompanied by profiles of all authors, about 200 Japanese characters (75 English words) for each author. The essential contribution of each author to the paper should also be included. Confirm that all persons who have made essential contribution to the paper are included.

8) Discussion with reviewers regarding the research paper content shall be done openly with name of reviewers disclosed, and the Editorial Board will edit the highlights of the review process to about 3,000 Japanese characters (1,200 English words) or a maximum of 2 pages. The edited discussion will be attached to the main body of the paper as a part of the article.

9) If there are reprinted figures, graphs or citations from other papers, permission for citation, if needed, should be clearly stated and the sources should be listed in the reference list. All verbatim quotations should be placed in quotation marks or marked clearly within the paper.

3.3 Format

1) The text should be in formal style. The section and subsection hapters should be enumerated. There should be one line space at the start of paragraph.

2) Figures, tables, and photographs should be enumerated. They should have a title and an explanation (about 20-40 Japanese characters or 10-20 English words), and the position in the text should be clearly indicated.

3) For figures, clear originals that can be used for printing or image files (resolution 350 dpi or higher) should be submitted. In principle, the final print will be 15 cm x 15 cm or smaller, in black and white.

4) For photographs, clear prints (color accepted) or image files should specify file types: tiff, jpeg, pdf, etc. explicitly (resolution 350 dpi or higher). In principle, the final print will be 7.2 cm x 7.2 cm or smaller, in black and white.

5) References should be listed in order of citation in the main text.

Journal – [No.] Author(s): Title of article, Title of journal, Volume(Issue), Start page-End page (Year of publication).

Book – [No.] Author(s): Title of book, Start page-End page, Publisher, Place of Publication (Year of publication).

4 Submission

One printed copy or electronic file of manuscript should be submitted to the following address:

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The submitted article will not be returned.

5 Proofreading

Proofreading by author(s) of articles after typesetting is complete will be done once. In principle, only revisions or correction of printing errors are allowed in the proofreading stage.

6 Responsibility

The author(s) will be solely responsible for the content of the contributed article.

7 Copyright

The copyright of the articles published in “*Synthesiology*” and “*Synthesiology* English Edition” shall belong to the National Institute of Advanced Industrial Science and Technology(AIST).

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Letter from the editor

It is our great pleasure to hand you the third issue of *Synthesiology*. We have been able to publish diverse papers on *Type 2 Basic Research* from wide-ranging fields. We are grateful to the authors, the reviewers, and all those who have contributed to this issue.

A symposium commemorating the launch of *Synthesiology* was held in the Akihabara Convention Hall, Tokyo on May 13. Participants (particularly from the industrial field) filled the hall and the symposium was extremely worthwhile. I think it has reflected great interests from people of various fields, and we are grateful to the lecturers as well as all the people who attended.

In this symposium, a panel discussion was held in addition to lectures, and we have received many expectations and requests for *Synthesiology*. Many people pointed out the importance of “the scenario that leads to the social outlet” and “the synthetic methodology.” These are points that were particularly emphasized in launching *Synthesiology*, and are indeed the central issues of *Type 2 Basic Research*. They are also described as part of required items for the contents of the paper in *Synthesiology*.

In reviewing the papers and in discussions in the Editorial Board, I felt that the authors are struggling hard to come to terms with “What is *Type 2 Basic Research*?” Particularly, I think people are thinking very deeply to describe “the scenario that leads to social outlet.” Although it is common practice for researchers to think about what research they should do to

benefit the society, it is new for them to describe the process as a scenario.

On the other hand, the format of description has not yet been standardized for synthetic methodology. I believe there are two main issues. One is the fact that synthetic methodology for *Type 2 Basic Research* are extremely diverse, and the principle of the methodology has not yet been well understood. Second, even if it is built up as a methodology, it is not easy to describe the synthetic process of research. Although these might be sorted out as more issues of *Synthesiology* are published, it is necessary to continue active discussion of the methodology.

The world in the 21st century must develop sustainably as we face limitations on environment, resource, and energy. Therefore, we must have a methodology for *Type 2 Basic Research*, which is always conducted with social outlet in mind. *Synthesiology* has a mission to describe this methodology for researchers, technologists, producers, managers, and the society, to make sure that this knowledge should be shared widely.

I hope many researchers and technologists of wide-ranging fields will cooperate in creating this newborn journal through active submissions and discussions.

Senior Executive Editor
Naoto Kobayashi

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