

Synthesiology

English edition

Proposal for technology architecture analysis

Clean and practical oxidation using hydrogen peroxide

**Development of
plastic certified reference materials (CRMs) to
cope with restrictions on hazardous substances**

**Development of forging process for
magnesium alloy continuous cast bars**

Synthesiology editorial board

Highlights of the Papers in *Synthesiology* Volume 8 Issue 1 (Japanese version Feb. 2015)

Synthesiology is a journal that describes the objectives and social value of research activities that attempt to utilize the results in society, the specific scenarios and research procedures, and the process of synthesis and integration of elemental technologies. To allow the readers to see the value of the papers in a glance, the highlights of the papers characteristic to *Synthesiology* are extracted and presented by the Editorial Board.

Synthesiology Editorial Board

Proposal for technology architecture analysis

– Application of an analysis method to the development of car navigation systems –

Noumi (METI) *et al.* discuss the findings for methods and strategies in developing new products by mainly analyzing the combination of elemental technologies for car navigation systems that was researched and commercialized by Sumitomo Electric Industries, Ltd. The paper attempts to universalize a method to construct technology architecture construction as a methodology, by providing a diagram after analyzing and organizing the steps and methods of R&D from the viewpoint of technological management. The paper is expected to have some ripple effect throughout industries to increase the accuracy of R&D plans for new products.

Clean and practical oxidation using hydrogen peroxide

– Development of catalysis and application to fine chemicals –

Kon (AIST) *et al.* describe the research scenario for the synthesis and integration of elemental technologies for hydrogen peroxide oxidation technology that the authors have presented for the first time in the world as a typical and specific example of green sustainable chemistry. The descriptions are given from the development of a new catalyst as core research to the product development and manufacture at bench plant scale for the purpose of final product realization. This paper discusses the integrated chemical technology that addresses the importance of catalyst technology in the chemical industry, as well as the importance of alternative technologies and viewpoints that are necessary when realizing new catalyst technology for industry.

Development of plastic certified reference materials (CRMs) to cope with restrictions on hazardous substances

– CRMs for analysis of heavy metals and brominated flame retardants regulated by RoHS directive –

Hioki (AIST) *et al.* summarize the social background against which the plastic certified reference materials (CRMs) became necessary, the course from the perception of demand to the development of CRMs, the technological development to meet the demands, and the status of distribution of RMs as a contribution to society. The paper describes the strategies and processes by which the RMs for heavy metals and brominated flame retardants that can be used internationally were developed, in prompt response to the strong demand from the industries to urgently react to the RoHS directive.

Development of forging process for magnesium alloy continuous cast bars

– Forging process utilizing grain refinement –

There is a social demand for weight reduction of a wide range of industrial products from the perspective of resource and energy savings. Saito (AIST) *et al.* develop a low-temperature forging process of continuous cast bars of magnesium alloys that have the lightest weight among structural metal materials yet had been considered impossible to accomplish. The paper presents an example in which major contributions were made in cost reduction, decreased environmental load, and improved work environment. It particularly discusses the elemental technologies selected and the integration scenario in developing the forging process through close collaboration between AIST's basic core technology and corporate manufacturing technology.

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Proposal for technology architecture analysis

— Application of an analysis method to the development of car navigation systems —

Toshihiko NOMI^{1,2*} and Hirosaka IKEDA³

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Product development involves many element technologies, so methods that analyze the integration process are important for R&D management. This paper proposes a new method to analyze *technology architecture*: i.e., a method for determining how to combine element technologies, which takes into account relations between product function and element technologies, and the complementary or substitutive relations among these element technologies. We applied this method to the case of development of car navigation systems, where the combination of element technologies changed several times. From this example application of our method, we obtained important insights into the analysis of technology architecture.

Keywords : Innovation, R&D management, element technologies, complementary or substitutive relation, technology architecture, car navigation system

1 Introduction

Important points for innovation are not only developing element technologies but also developing a new way to integrate them. While the former is purely a technical subject, the latter is closely related to R&D management, and affects competitiveness of finished products. This brings the following questions. How should we select a technology from candidate technologies? How should we develop the way to integrate many element technologies? In order to reply to these questions, it is important to study the past innovation cases, and to accumulate those case studies.

This paper analyzes the way to combine element technologies as “technology architecture.” The word “architecture” has been used in the field of system engineering as a technical term which expresses fundamental structures of the relation of functions or performance of a total system and sub-systems composing it or relation among the sub-systems. These days, the term is also used in business administration studies^[1] and is attracting attention in technological management studies. However, attention has not been paid to the fact that the way to integrate element technologies is a management issue to be selected artificially in the process of R&D. We propose a new method for illustrating and examining the technological relation of a total system (a finished product) and element technologies, and the technological relation among element technologies, by using the new word “technology architecture.” Moreover, we apply this method to the case of development of car navigation systems by Sumitomo Electric Industries Ltd. (hereinafter “Sumitomo Electric”). Sumitomo Electric was a leading

company in the changing of generations of car navigation systems in the beginning, especially in developing the current location detection technologies. From this application example of our method, we obtained important insights into the analysis of technology architecture.

This paper describes the authors’ views and is not the official views of the organization to which the authors belong.

2 Prior research and issues of this study

Technological methods changed in the development of car navigation systems as shown later. For such innovation, we should keep in mind the fact that technological issues change in the life cycle of technology or industry. Abernathy and Utterback pointed out that product innovations were essential in the early stage of new industry where many types of products came onto the market by using many types of technologies, but product design gradually shifted to a “dominant design,” and process innovation became main after the dominant design appeared.^{[2][3]} Foster said that technologies developed along an S curve, and a new type of technology was needed to break through the limit when old types of technology matured and came close to the limit of performance.^[4]

Although innovations are often divided into the two types of incremental and radical innovations, Henderson and Clark categorized them into four types using two axes, depending on whether core concepts were reinforced or overturned and whether linkages between core concepts and components were unchanged or changed,^[5] as shown in Fig. 1. Although

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in the “modular innovation” type in the figure, components using new technology substitute the old, in the “architectural innovation” type, core concepts of components do not change but the architecture of product design changes, and it means that changes of the relation among components make an innovation even though we use old components. They pointed out that “architectural innovation” changes the technical paradigm citing the semiconductor lithography industry as an example, and emphasized the importance of this type of innovation because change of the technical paradigm brings about the change of the competitive company from one to another as shown by Tushman and Anderson.^[6] Their study has similarities with this paper in terms of focusing on “architecture.” However, they think “radical innovation” is different from “architecture innovation,” although examining architecture is indispensable for planning radical innovation. In this paper, we analyze the technology architecture including the case of radical innovation without being concerned with the classification of Fig. 1. Moreover, we analyze what technology architecture is appropriate and how to examine it, as we think these issues are important.

On the other hand, there is much research on “product architecture” in the field of business administration.^{[1][7]-[10]} They classify products into two types, “modular architecture” where one module bears one function and “integral architecture” where it does not, and analyze competitiveness of firms or appropriate strategies based on this typology. But, issue awareness of this paper is different from the above approach.

| | | | |
|---|-----------|--------------------------|--------------------|
| | | Core Concepts | |
| | | Reinforced | Overturned |
| Linkages between Core Concepts and Components | Changed | Incremental Innovation | Modular Innovation |
| | Unchanged | Architectural Innovation | Radical Innovation |

Fig. 1 Typology of Innovation by Henderson and Clark^[5]

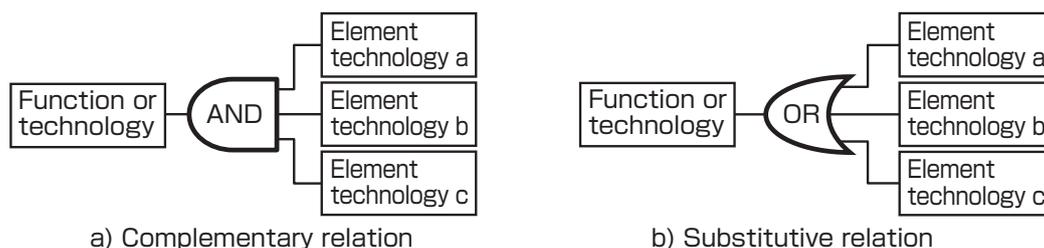


Fig. 2 Complementary and substitutive relations among element technologies

“Technology architecture analysis” in this paper is a method to examine the way to integrate element technologies which researchers or engineers need for arranging R&D plans of new products. “Technology architecture” is not fixed technologically, but is to be designed and selected by researchers or engineers. It is related to the studies on business administration, because the result of the selection affects relations among firms and competitiveness of firms. However, how to examine technology architecture is an independent research topic.

3 Method to illustrate technology architecture

Performance of a system product can be broken down to some functions necessary to the performance, and each function is realized by one or several element technologies. When several element technologies are needed for realizing one function, these element technologies have complimentary relations with each other. When there are several candidate element technologies to realize a function and any one candidate technology can realize it, these element technologies have substitutive relations or competitive relations. Only one element technology is selected from these candidates when development of a new product is completed. However, which substitutive element technology should be selected is an important issue for management when planning R&D. Therefore, this paper analyzes substitutive element technologies explicitly. We use logic symbols “AND” and “OR” to illustrate complimentary and substitutive relations among element technologies, as shown in Fig. 2.

Moreover, products often evolve as time goes by, and their element technologies also change. One type of change is brought about by an addition of a new function, and a new element technology is also added for that purpose. This change can be illustrated by using “AND” and “OR” as shown in Fig. 3 a). However, this is complicated. It would be better to illustrate it as Fig. 3 b) by bringing in a new symbol “ADD↓.” Additionally, another type of change of element technology is replacement by a different element technology which has a substitutive relation with the old technology due to technological progress. Although this type of change is basically a phenomenon within the relation shown by “OR,” we illustrate it by introducing a new symbol “OR↓” as in Fig. 4, when we stress change with time. As mentioned above,

this paper illustrates the technology architecture basically by using logic symbols “AND” and “OR,” with additional new symbols “ADD↓” and “OR↓.” When considering chronological changes in a product or element technologies, there is only “AND,” not “AND↓” for a line of AND, “OR” and “OR↓” for a line of OR, and there is “ADD↓,” not “ADD” for a line of ADD.

Furthermore, the direction from left to right in the figures means breakdown from the whole to the element. The figures have a holonic structure, and they can be used in more detailed element analysis, or analysis of large whole systems.

4 The case of car navigation system development by Sumitomo Electric

4.1 R&D issues in developing car navigation systems

Navigation systems detect current locations of vehicles correctly (the first fundamental function) and provide guides to destinations (the second fundamental function).^[11] They have been used for ships from old times, and are used widely for aircraft in modern times. However, they had not been used for automobiles before 1980, because requirement for technology to detect current locations in automotive use was much more demanding than in marine or flight use. Concretely speaking, firstly, the margin of error in detecting current locations must be very small, because accurate locations, such as of intersections or gateways of expressways, are critical. Secondly, the price of equipment for automobile use must be very low compared to those of gyroscopes for military planes which vary from several millions to several

tens of million yen.^[12] Thirdly, operation must be easy for automobile drivers, unlike professional pilots for marine and flight use.

Meanwhile, there are two types of technology systems for navigation in marine and flight equipment, which are self-contained^{Term 1} and heteronomy^{Term 2} navigations. Self-contained navigation is a method that measures the distance and direction of locomotion, and the current location is reached by adding these measurements to the starting position and direction (Fig. 5). Heteronomy navigation is radio navigation^{Term 3} from a station on the ground which transmits location information when a vehicle comes close to it. However, no station on the ground with this function existed then for automobiles.^[13]

As explained above, high-performance and low-cost were required for car navigation systems although its technological seeds were limited, and they were not realized for a long time. However, the feasibility of its business emerged by the advance of relevant technologies in the 1980s. An important technological advancement was the invention of “map-matching technology,^{Term 6}” which was developed in 1983 by ETAK, a venture business company in the U.S. This is a technology to correct an error on software by comparing detected trajectory and current location with roads on a map assuming that cars must run on roads. Although the self-contained navigation needed high-precision sensors because measurement errors were accumulated as moving distance increased, the requirement for precision of sensors was moderated by this technology.^[13] In addition, some small-

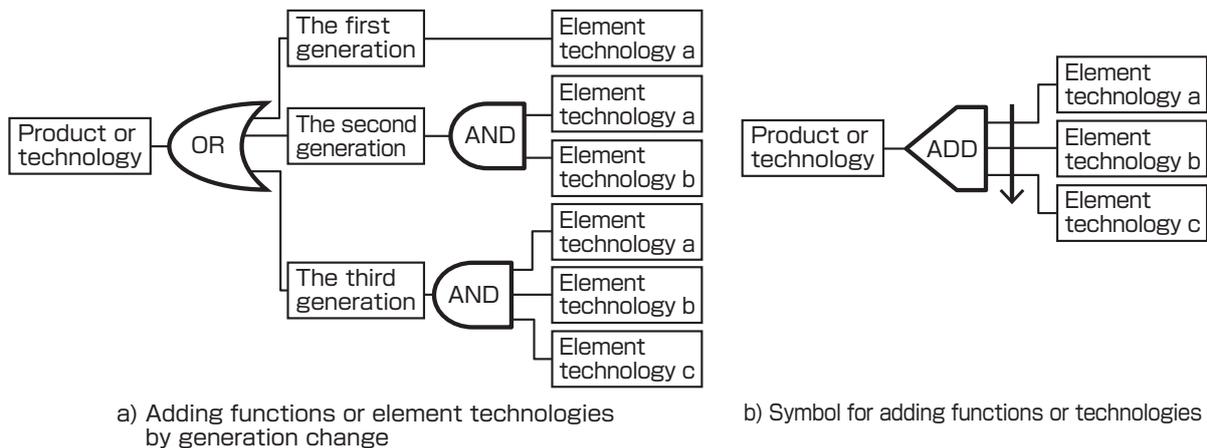


Fig. 3 Symbol “ADD↓”

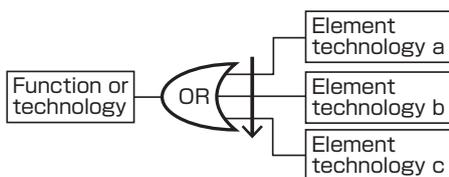


Fig. 4 Change among substitutive element technologies with time (OR↓)

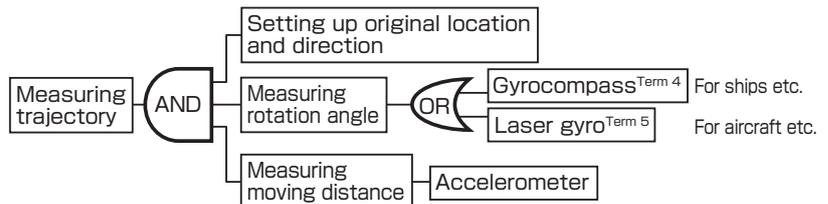


Fig. 5 Former method to measure trajectory by self-contained navigation

sized and highly-efficient information appliances, such as CD-ROMs and 16bit-CPU, were developed in the 1980s.

Some companies had started to develop car navigation systems. There are three generations in car navigation systems. The first generation detects only the current location, the second generation additionally provide route guides to destinations, and the third generation provide route guides by receiving real-time information, such as traffic jams, road repairs and traffic accidents, from outside (Fig. 6). Car navigation systems have evolved through these changes of generations. This paper analyzes the birth and changes in the technology architecture of car navigation systems as follows.

In order to develop a car navigation system, R&D of current

location detection technologies is necessary, as well as that of hardware and software to control the system. There are a variety of current location detection technologies such as self-contained navigation, GPS, radio navigation from a ground station, and a combination of these systems.^[14] In the case of self-contained navigation using map-matching technology, sensor technologies and digital road maps are indispensable. Detailed R&D issues are arranged in order in Fig. 7. This figure describes the fundamental structure of the technology architecture including new technology types which had not been developed in the beginning of the 1980s, which are explained later, because we arranged them in retrospect. R&D issues on hardware including sensors are indicated in Fig. 8, and it was decided that many components would be supplied from the outside. Regarding software, R&D on software was needed for displaying the road map,

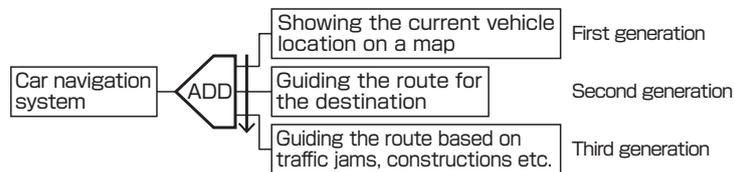


Fig. 6 First-third generations of car navigation systems

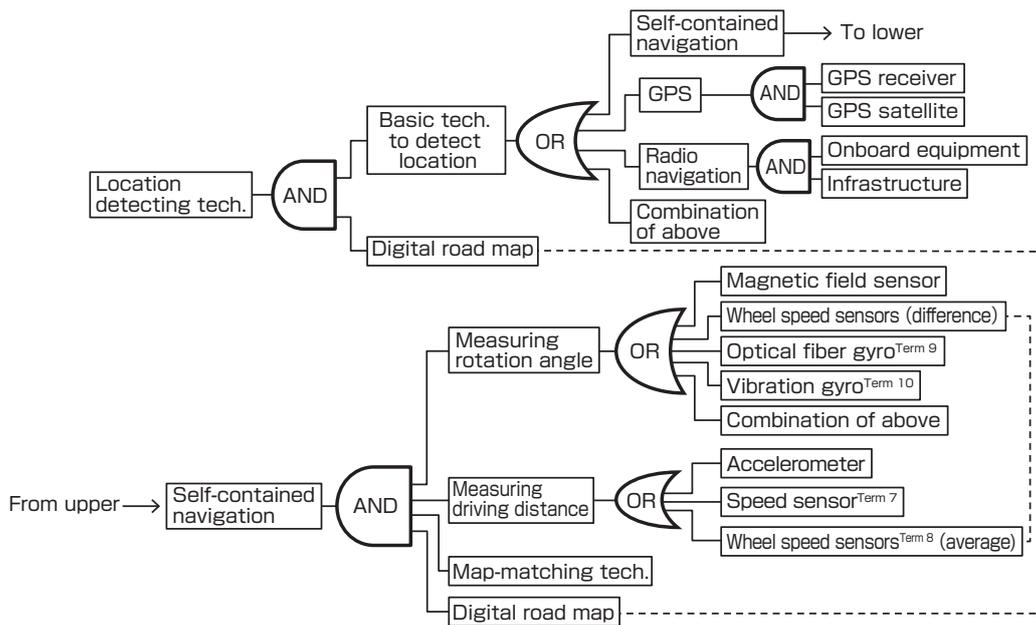


Fig. 7 R&D issues for detecting current location of car navigation systems (Technology architecture)

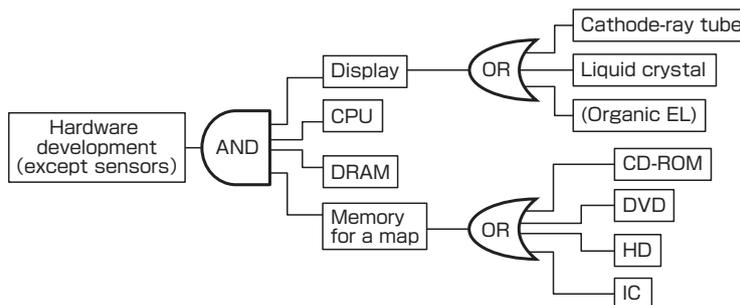


Fig. 8 Element technologies for hardware development

for controlling the car navigation system by a driver, as well as for detecting the current location. Software to calculate the route was also necessary after the second generation.

4.2 The first development of a car navigation system by Sumitomo Electric (The first half term of the first generation)

Sumitomo Electric focused on the map-matching technology developed by ETAK, and considered introducing the technology. However, it launched R&D on a car navigation system by itself in 1983 because technology in the U.S. was not conformed to the traffic conditions in Japan. The company set its target on a total system in which measurement errors should be within several tens of meters and should not miss a road, and the price should be around 300-400 thousand yen.

For the fundamental current location detection technology, only self-contained navigation was a realistic choice because GPS was not available due to the small number of GPS satellites, and radio navigation was also not possible because there were no ground stations. The basic strategy was to use map-matching technology for self-contained navigation, because target performance mentioned above was very difficult in those days. Additionally, sensors had to be very accurate, and digital road maps had to contain detailed road information in order to realize correct map-matching.

Rotation angle sensors and travel distance measuring sensors were necessary as sensor technologies, and there was not a wide range of alternatives in those days as shown in Fig. 9, except for extremely expensive sensors. Sumitomo Electric used a magnetic field sensor for measuring the rotation angle, but, using it solely was insufficient because disorder occurred near large constructions or DC drive trains. Sumitomo Electric, which was manufacturing anti-lock braking systems (ABS), knew that luxury cars had wheel speed sensors,^[13] got an idea that rotation angle could be measured by the difference between numbers of revolutions of right and left wheels, and decided to develop a system using wheel speed sensors for combined use with a magnetic field sensor. The reason for combining two kinds of sensors is to use two kinds of information complementally, because with wheel speed sensors, errors caused by wheel slip or change of tire inflation

pressure also occurred. It was decided that information about travel distance would be obtained from the average speed of both wheels.

For developing a digital road map, there were two choices of 1:25,000 maps or 1:2,500 maps. The former maps for the whole of Japan could be obtained all together, because the Geospatial Information Authority of Japan had them. However, they did not include information about community roads. Sumitomo Electric decided to use 1:2,500 maps in three metropolitan areas, because high precision maps were important for the map-matching technology. Local governments of cities, towns and villages had 1:2,500 maps for urban planning, therefore Sumitomo Electric negotiated with them, such as the 23 wards of Tokyo, to use the maps. However, some of these maps had old information because they were issued a long time ago. Therefore, it decided to also use the detailed maps for cables or pipe construction owned by power companies and gas companies. It digitalized information of these road maps with a large amount of labor by using a great deal of money.

For necessary hardware excepting sensors, such as displays, CPUs, memories for digital road maps and DRAMs, it decided to procure good ones from other companies. Concretely speaking, it decided to use around 6 inch cathode-ray tubes for displays, CD-ROMs for road map memories, and it used cushioning rubber for CD-drive to bear the vibration of automobiles.

Some software was also necessary, such as software to control information from wheel speed sensors, magnetic field sensors, and information about travel distance, and to conduct map-matching by combining the information with a digital road map, software to show calculated current location on the display, and software to give current location set up by a driver feedback to the system. Thus data processing was very complicated, and on-board CPU needed much time for processing. However, the target time in which the system should display the vehicle location on the display was set as within 0.3 seconds. For this purpose, the arrangement of road map data was changed to quicken readout time, a good calculation method for map-matching was sought, and an original OS to increase the data processing speed was

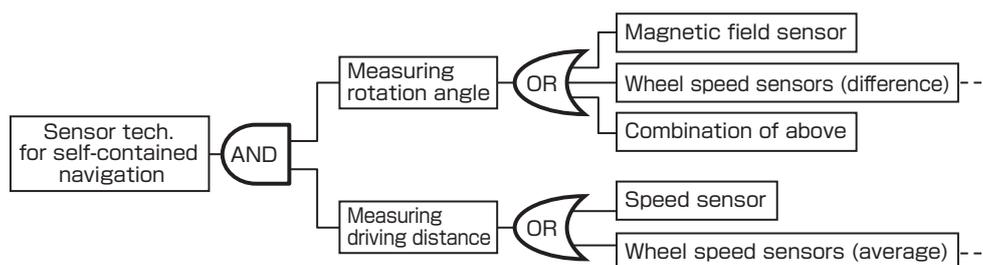


Fig. 9 The choice for sensor technologies in the first development of a car navigation system

developed. Finally, it cleared the target time. Additionally, a car navigation system needed software to control and display air-conditioners and car-audio systems, because large displays of car navigation systems would be installed at the place where switches and displays of air-conditioners and car-audio systems used to be.

Technology architecture mentioned above is shown in Fig. 10. After developing element technologies, Sumitomo Electric made a trial product that integrated element technologies, attached it to a real vehicle, and conducted experiments by a running vehicle. The most difficult problem with integrating element technologies into a total system was calculations of the current location in a condition that there was no absolutely reliable information, because sensors had measurement errors which were very large sometimes, and information of road maps was old and sometimes different from actual roads. In order to solve this problem, it decided to stochastically use all information from each sensor, a digital road map, and trajectory information up to that time, and set the extent of credibility of such information individually within the software. For this purpose, it repeated trials and errors, i.e. extracted problems by a real running vehicle test, refined the software, and conducted tests again. However, it used computer simulation in the laboratory frequently by using data collected from real running vehicle tests after the first test. It improved the accuracy of detecting the current location by the cycle of refining, testing a trial product, and extracting problems. This sequence yielded its own map-matching technology within Sumitomo Electric.^[13]

The car navigation system as a result of such R&D put map-matching technology into practical use for the first time. The system became so reliable that frequency for a driver to reset the current vehicle location on the system when it missed a road was decreased to once per 40-50 km drive. This system had the best performance in the world those days, and was adopted by Nissan Motor Corp., and put into practical use by being installed in the 1989 model of Nissan Cedric and Cima.

On the other hand, drivers became to trust the car navigation system, therefore they began to complain about mistakes in current locations. The mistakes were mainly caused by insufficient accuracy of the measuring rotation angle. Even though the accuracy of wheel speed sensors was of a high level, it became clear that it was lower than the market needs.

4.3 Development in the latter half term of the first generation by using an optical fiber gyroscope

Sumitomo Electric launched plans to develop the next system just after the development of the system in 1989. The most important challenge was to develop a more accurate rotation angle sensor than the wheel speed sensors. In those days, Sumitomo Electric had developed an optical fiber gyroscope by itself, whose accuracy in measuring the rotation angle was very high, however its sample price was some million yen, which had to be reduced to 10-20 thousand yen for automobile use. Sumitomo Electric reconsidered one by one its element technologies, such as materials of the parts, the process technologies, and finally it realized this price. While the technology architecture of this system was basically the

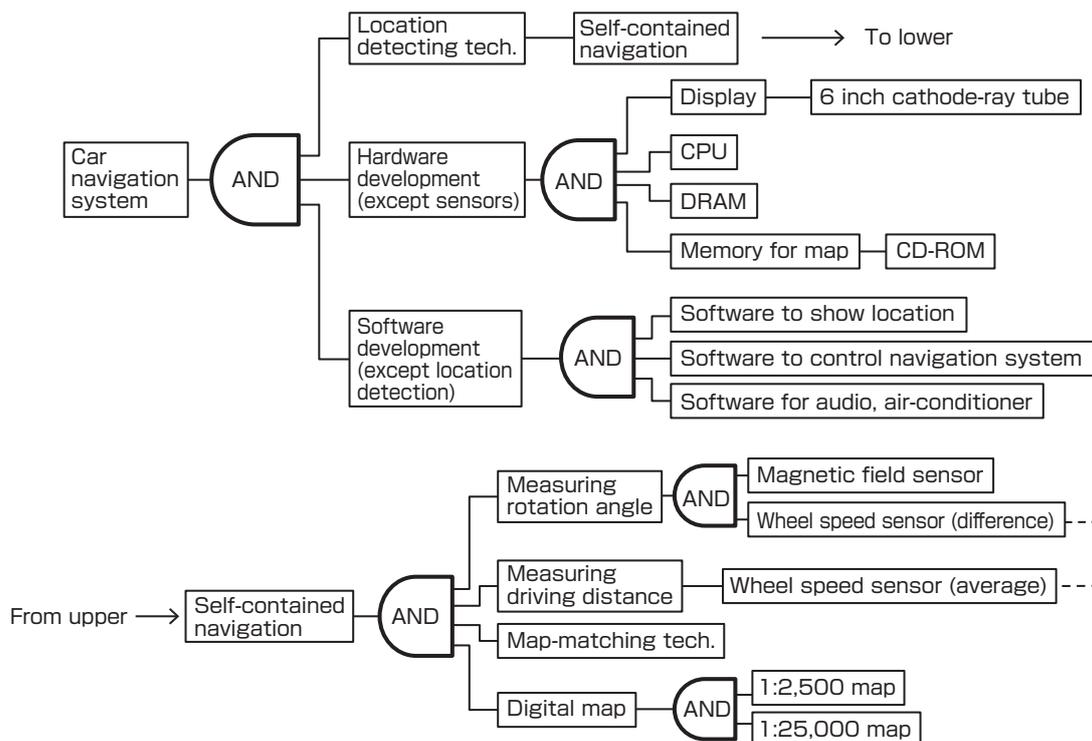


Fig. 10 Technology architecture when the first car navigation system was finished (1989 model)

same as the previous system, the combination of sensors for self-contained navigation was changed as shown in Fig. 11.

On the other hand, except for the design on the display, it used the digital road map developed by the Japan Digital Road Map Association established in 1988, which was developing the digital road map associated with related government offices and companies concerned.

The car navigation system of the latter model of the first generation, which was developed as explained above, was installed into the 1991 models of Nissan Cedric and Cima. Although other companies followed Sumitomo Electric in the production of car navigation systems by using map-matching technology, the optical fiber gyroscope, which was not installed into other companies' products, became the source of competitive advantage of the Sumitomo Electric's product, which decreased the frequency of reset of current vehicle location by a driver into once per about 200 km drive.

4.4 Development of the second generation which became the dominant design

One of the next challenges was to add the function of guiding toward a destination (the second fundamental function of navigation) on the previous function of detecting the current vehicle location. Another company preceded in the development of such a second generation car navigation system, therefore Sumitomo Electric also had to follow. Then, it was necessary to develop software to calculate the route guide, and to add traffic control information such as one-way streets or no right turns and road connection information such as connecting roads to expressways on the digital road map. Many universities had published algorithms for calculation software, however a large memory capacity and high speed read-out capacity were needed. Sumitomo Electric developed its own route guide software in order to calculate the route at high speed by a small memory capacity,

Additionally, other challenges were to incorporate the fruits of technology progress in the relevant fields; one of these was GPS. The designers of car navigation systems were looking for a way to know the absolute position, because offset of position which resulted in missing a road could not be avoided entirely even when map-matching technology was used. However, GPS made it possible, which is the

technology to know the absolute position of a vehicle by receiving positioning signals from 4 GPS satellites of the 24 GPS satellites located in orbit.^{[15][16]} After its launch in 1978, although the number of GPS satellites was small in the 1980s, it became large enough for practical use in the 1990s.^[17] Another company put a car navigation system using GPS into practical use in 1990, therefore Sumitomo Electric decided to use GPS. Issues for R&D were mainly to develop software for map-matching using information from GPS, because GPS receivers were already distributed in the market. (Thereafter, establishment of GPS was announced in 1993, and its full-scale service was started in 1995.) Although GPS had problems that it was not available in tunnels or behind buildings, and that its margin of error was 100m at maximum because the U.S. Department of Defense lowered its precision intentionally as selective availability (S.A.) measures, combined with self-contained navigation, problems in practical use could be avoided.

Another technology incorporated from the fruits in the relevant field was a vibration gyroscope which was used for measuring the rotation angle. This is based on the principle that inertia of solids of revolution (Coriolis effect) is also effective against oscillating bodies, and the technology to refine its sensibility to the practical level was developed in 1988. Downsizing and cost reduction was also achieved later.^[12] This technology began to spread for use in hand-shake prevention systems of cameras. Sumitomo Electric took note of this, and decided to use a small and low-cost vibration gyroscope for its car navigation system, although its accuracy was lower than the optical fiber gyroscope, because accuracy required for a rotation angle sensor became lower when used jointly with GPS. A magnetic field sensor was no longer needed. However, a vibration sensor had a problem of zero-point temperature drift where the sensor displays a rotating signal even when it is not rotating caused mainly by temperature. Although this was not a problem for camera use, temperature correction was needed for a car navigation use. Therefore, Sumitomo Electric requested Murata Manufacturing Co. Ltd. a vibration gyroscope manufacturer, to reduce the drift, and the company achieved this^[13] (as shown in Fig. 12).

Thus, the second generation of car navigation systems, whose cost reduction and downsizing were realized through

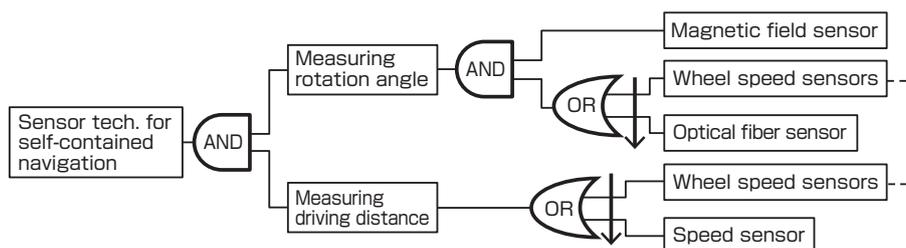


Fig. 11 Change of sensors from 1989 model to 1991 model

the development mentioned above, was adopted in the 1992 model of Diamante of Mitsubishi Motors. Thereafter, the mode to use GPS and a vibration gyroscope jointly in a car navigation system diffused among other manufacturers, and this style became the industry-wide standard, i.e. the dominant design around 1993.

4.5 Development of the third generation of car navigation system and the withdrawal of Sumitomo Electric

In the 1990s, car navigation systems diffused widely. The technology progress brought about the third generation, which gave route guides by taking into account traffic information such as traffic jams, accidents and road constructions. For this generation, it was necessary for real-time traffic information to be offered from the outside (the ground stations) to vehicles running on the road. Therefore the Vehicle Information and Communication System

Center (VICS^{Term 11} center) was established in 1995, after careful consideration from 1990. This center collects traffic information from the police and road administrators, and offer the information to car navigation systems on-board by optical beacons^{Term 12} or radio wave beacons.^{Term 13} It started the infrastructure development i.e. installation of the stations on the roads to offer the information, launched the service in Tokyo and Osaka metropolitan areas from 1996, and expanded the service area thereafter. From the beginning of this service, the car navigation systems of Sumitomo Electric also evolved into the third generation, and used VICS information. VICS information was also useful for detecting the current location, and it was used jointly with GPS and a vibration gyroscope (as shown in Fig. 13).

However, GPS receivers, vibration gyroscopes, and VICS receivers no longer were competitive advantages for a car

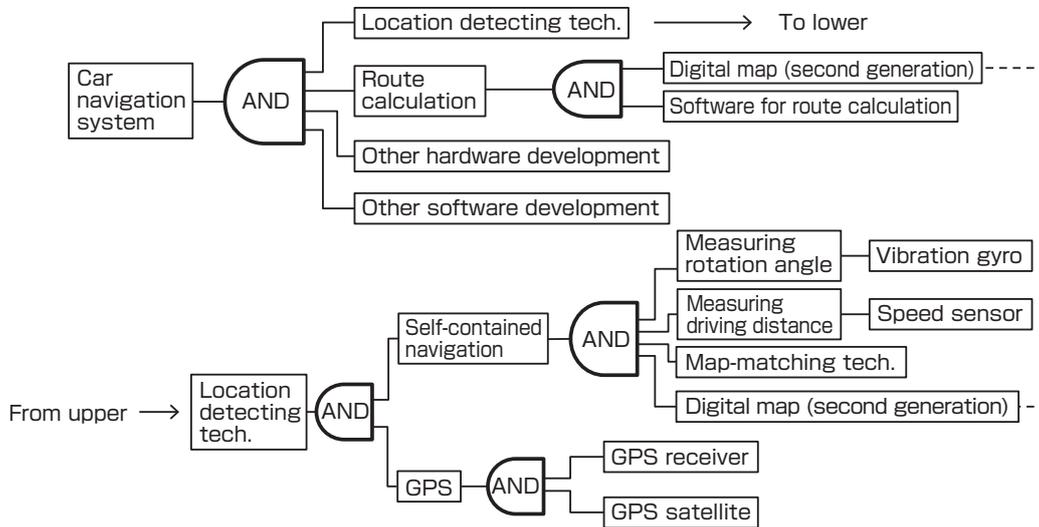


Fig. 12 Technology architecture of 1992 model (second generation)

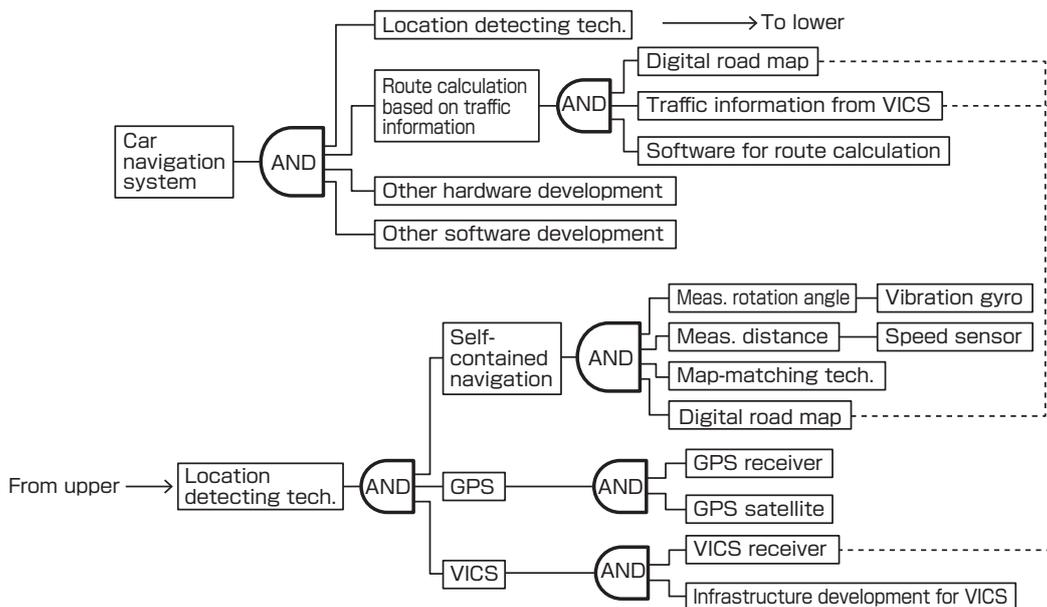


Fig. 13 Technology architecture of the third generation of car navigation systems

navigation system manufacturer, because anyone could purchase them from companies specializing in making these pieces of equipment. As a result, the number of companies entering the car navigation system business increased to twenty or more by mid-1990s, and their product prices dropped. Sumitomo Electric also became caught up in the competition for lower prices. On the other hand, the expansion of the functions to be processed by software led to sharp increase in the scale of software, manpower for its development and development cost. Original OS introduced for speeding up data processing in the beginning of the development of the car navigation system also enhanced this tendency, and brought a disadvantage in the competition with companies who used a general-purpose OS. Owing to continual deficits in the business, Sumitomo Electric was forced to withdraw from the car navigation system business in 2000 following a decision made in 1999.

5 Analyses of technology architecture from a short term perspective and innovations over a long time frame

In the previous chapter, this paper explained the facts of how Sumitomo Electric made the selection of element technologies in the period of the emergence and the generation change of car navigation systems. This story can be interpreted not only as four short-term cases of 4 R&D projects, i.e., the first half term of the first generation, the latter half of the first generation, the second generation and the third generation, but also as one long-term case of the evolution process of car navigation systems. Therefore, this chapter focuses on the examination from these two viewpoints.

5.1 How to examine an R&D plan of a new product in each generation

The examining process is a focal point when planning R&D of new products from a short-term perspective. In the case of car navigation systems, Sumitomo Electric examined ① system configuration of how the total system consists of sub-systems, i.e. element technologies, ② broad search of candidate technologies to realize each sub-system, ③ appropriate selection of technologies by comparison of candidate technologies, ④ deciding between in-house development and acquisition from the outside for each adopted technology. This means that the following 4 processes are examined in the technology architecture analysis, i.e. ① examination of complementary technologies, ② quest for substitutive technologies, ③ selection of substitutive technologies, ④ examination of the ways to obtain element technologies. When considering R&D plans, it is important to draw up a figure of technology architecture according to these 4 processes, and to examine the 4 processes deeply by using the figure. Additionally, the following knowledge about examination of these 4

processes have been gained from the case of car navigation development.

Firstly, it is important to examine both complementary technologies and substitutive technologies as element technologies. The technology architecture for a finished product, such as Fig.10, 12 or 13, is written by only “AND,” because a finished product does not include an unnecessary element, and consists of only complementary technologies. However, this is the result after selecting element technologies to be adopted. When examining an R&D plan, it is important to specify substitutive technologies as candidates as shown in Fig.7 or 9, and to select appropriate technologies. Actually, Sumitomo Electric had competitive advantage because it selected suitable element technologies such as map-matching technology with wheel speed sensors or an optical fiber gyroscope by taking product differentiation into account.

Secondly, it is critical to collect a wide variety of information about substitutive technologies to be listed up as candidates. The information about rotation angle sensors in the car navigation case was of 4 types, i.e. original idea for wheel speed sensors, in-house technology for an optical fiber gyroscope, information from a competitor for GPS, and information from other industry (camera industry) for a vibration gyroscope. Although generally, there is an argument on which is more important, exploration for candidate technologies or exploitation of existing technologies, Sumitomo Electric carried out exploration appropriately.^[19] Some research on dynamic capability of companies also points out the importance of sensitivity for detecting new opportunities.^[20]

The third point concerns the standard in selecting element technologies. An element technology should be selected not only by performance and cost of the technology, but also by the competitiveness of the finished product with the technology installed, or, in other words, the relation between the whole and elements. For example, the reason for adopting an expensive optical fiber gyroscope in the 1991 model was to respond to the market needs for the product. On the other hand, sometimes complementary technologies used together affect the selection of element technologies, in other words, the relation among elements. For example, detailed road information from 1:2,500 maps was input into digital maps in the 1989 model in order to bring out the best in map-matching technology. A vibration gyroscope was adopted instead of an optical fiber gyroscope in the second generation system because requirement for the accuracy of a rotation angle sensor was relaxed by the use of GPS.

The fourth point is the possibility of using substitutive technologies complementarily. Although a magnetic field sensor and wheel speed sensors are substitutive for rotation

angle sensors, they were used complementarily in the 1989 model in order to compensate the different defects of each technology. The relation between GPS and self-contained navigation was the same as above.

The fifth point is the variety of ways to obtain element technologies. There were in-house developments, purchase of hardware such as information appliances from other companies, and a request to another company for the development of vibration gyroscope. Introduction of map-matching technology from a venture company and technology transfer of route guide software from universities was also considered, although they were not realized in the end.

The sixth point is that not only examination before R&D but also tests and improvements after development of element technologies and trial production of a total system are important, and these processes should be prearranged in an R&D plan. There is possibility of some omissions of complementary technologies in an R&D plan, although it should include all necessary complementary technologies. There is also possibility that a total system cannot achieve its designed performance when all element technologies are combined. In the case of car navigation, repeating trials and errors brought out much improvement in the performance when testing a trial car navigation system installed on a real running vehicle.

The first, second and third points above are deemed to be

especially important. Although these points are critical for deciding element technologies, element technologies are not necessarily to be decided uniquely by technology architecture analysis. For example, one set of element technologies is not always to be extracted when functions of a product are broken down to element technologies from the first viewpoint. Therefore, examination from many angles would be necessary.

5.2 Innovations of technology architecture over a long term

Interpreting this story as one long-term process from the emergence of a car navigation system business until the appearance of its dominant design, innovations of the technology architecture can be drawn as Fig.14.

There are two types of innovation of the technology architecture as shown in Fig.14. One type is expanding the functions of the product, and adding necessary element technologies. When a car navigation system converted from the first generation which had only the function to show the current vehicle location on a road map to the second generation which had a function to guide the way to a destination too, software to calculate the route and traffic control information such as one-way streets and no right turns in a digital road map became necessary. Moreover, when changing to the third generation which took account of traffic information such as traffic jams and road constructions, transmitting and receiving real-time information through VICS between the onboard navigation

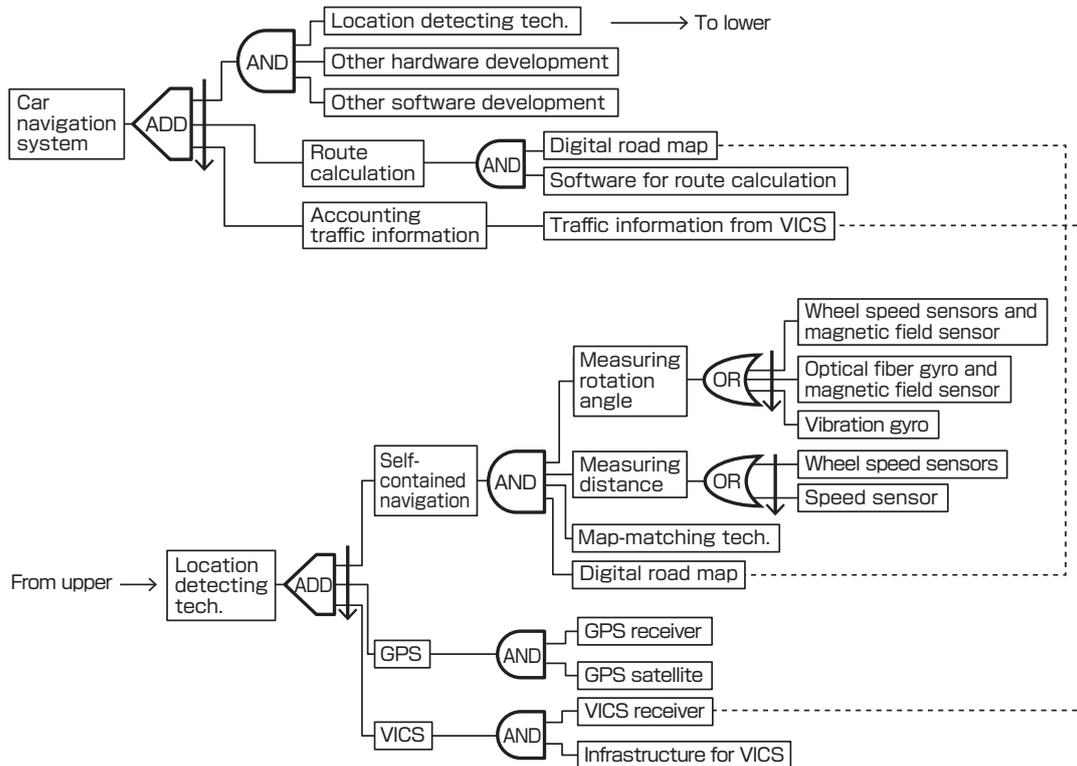


Fig. 14 Innovations in technology architecture of car navigation systems

system and infrastructure outside the vehicle became necessary. The symbol “ADD↓” shows this type in Fig.14. Another type is innovation of technology architecture replacing technology seeds or technology types. For example, the rotation angle sensor changed from joint use of wheel speed sensors and a magnetic field sensor to joint use of an optical fiber gyroscope and a magnetic field sensor, and then to a vibration gyroscope. The symbol “OR↓” shows this type in Fig.14.

A characteristic in the innovation of car navigation systems is that the direction of technology evolution depended on the relation between product performance and market needs. In concrete terms, performance of the rotation angle sensors was more important than their cost in the early period of the business, for example the wheel speed sensors were used in addition to a magnetic field sensor, or the expensive optical fiber gyroscope was used. On the other hand, the cost was more important than the performance of the sensors in the period of the second generation which used GPS, as shown in the adoption of a small and low-cost vibration gyroscope in spite of its lower performance. This story is similar to the “destructive innovation” of the hard disk drive industry in which 8 inch drive, which was the mainstream in the market, shifted to lower performance products such as 5.25 inch drive or to 3 inch drive.^{[21][22]}

Additionally, there would be differences in the details to be studied of the R&D plan between a long-term viewpoint (Fig.7) and a short-term viewpoint (Fig.9). In 1983 when Sumitomo Electric launched R&D on a car navigation system, the use of GPS was not realistic, because the infrastructure of GPS, i.e. enough number of GPS satellites, was not yet arranged although its plan had been announced. At the time, the use of radio navigation was neither realistic, because the infrastructure of VICS was not planned although its technology was well known. Therefore, it was rational to narrow the study down to R&D plans on a self-contained navigation and its sensors from a short-term viewpoint as shown in Fig.9. However, from a long-term viewpoint, the technology architecture of car navigation systems changed at once when a breakthrough occurred to remove bottlenecks of technologies or social conditions. Fig.7 is the figure of the technology architecture containing wide-range substitutive technologies including candidate technologies mentioned above. As one hypothesis, it would be useful to identify bottlenecks of technologies and to simulate the change of technology architecture when the bottlenecks are eliminated.

In the simulation, it is not necessary to know the specific way for breakthroughs. Through this simulation, companies could become sensitive to risks and chances that emerge in long-term technological changes, and could react positively to the changes thereafter.

In the case of car navigation, there was a change in the competitiveness of companies along with the change of technology architecture as shown in Fig.15. In concrete terms, the sensor technology owned by Sumitomo Electric lost its competitiveness, and capabilities to develop software became a key in the competition among companies after the current vehicle location could be detected by a GPS receiver and a vibration gyroscope purchased from other companies. Industry shifts from a birth period to a maturing period through a growth period when many companies enter the industry and their competition becomes severe. A successful company in the maturing stage is not necessarily a leader company in the beginning.^[23] If a company could anticipate the changes of technology architecture based on the above hypothesis, it would be useful for a long-term technology management, although this is a future research theme.

6 Conclusion

This paper proposed the methods to illustrate and analyze technology architecture, and applied them to the case of the innovation of car navigation systems by Sumitomo Electric. It showed that this illustrating method could express technology architecture objectively, and could express changes in element technologies in past innovations. For example, although it is difficult to understand the whole structure with many element technologies related to the current vehicle location detection in the case study, relations among element technologies become clear by illustration as shown in Fig.7. A prior examination on an R&D plan would become easier by this means. This is the fundamental function of technology architecture analysis.

Additionally, we learnt many lessons on prior examination for short-term R&D projects from this case study, and could present one hypothesis on the method to apply to long-term R&D management which included generational changes of products. Technology architecture is a subject for researchers or engineers to design and choose, therefore this method is expected to be used in prior examination of R&D plans. This method would be useful for examining what functions finished products should have, and what element technologies

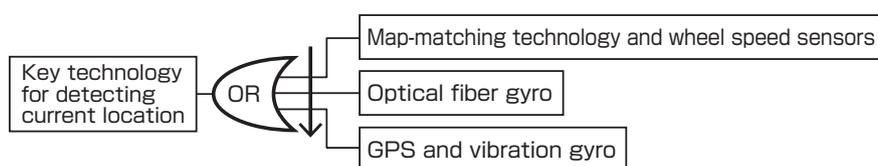


Fig. 15 Change of key element tech. for detecting current location

should be developed therefor, for example, in development of intelligent transport systems (ITS)^{Term 14} which is an advanced form of car navigation systems, or in development of robots which are used in real-life settings such as nursing care, or in the field of agriculture, forestry and fishing.

Furthermore, it would be meaningful when management and researchers/engineers exchange opinions about strategies for a technology choice or about possible expansion of products/technologies in the future, to illustrate technology architecture and to show various routes connecting a finished product and element technologies including substitutive technologies that may look impractical in a short-term.

Technology architecture analysis also has possibility to be helpful in discussions with management on business strategies considering market size and profitability as well as technology strategies which are also important. A technology strategy for a technology choice or for the way to obtain parts or element technologies has possibility to influence the industrial structure in the future, and profitability depends on the industrial structure such as price bargaining power with user companies or suppliers and the new entry by competitors after industrialization. Hence, an integrated framework to examine technology architecture, a technology strategy, future industrial structure and a business strategy might be possible, and this is a future research theme. Moreover, technology architecture might be related to a path for evolution of element technologies or to core technology strategies. These are also subjects for future research. Therefore, it is important to apply technology architecture analysis to various cases in the future, and to accumulate the knowledge.

Terminologies

- Term 1. Self-contained navigation: One kind of navigation technique to detect the current location by only equipment installed in vehicles such as automobiles. For that purpose, dead-reckoning technique is usually used. It detects the current location by adding the measured rotation angle and the driving distance of the vehicle to the original or starting location and direction.
- Term 2. Heteronomy navigation: One kind of navigation technique different from self-contained navigation. A vehicle detects the current location by receiving information transmitted from the station on the ground etc.
- Term 3. Radio navigation: One kind of heteronomy navigation. The vehicle detects the current location by receiving radio wave information from a station, when a vehicle comes close to a station.
- Term 4. A gyrocompass: A device to know the direction by using the nature of a fast-spinning object, which keeps the rotation axis in the original direction.
- Term 5. A laser gyroscope: A device to measure the angular velocity of rotation using a characteristic of lasers that the propagation velocity changes by rotation, which has a laser oscillator structure with ring-like optical waveguide consisting of several mirrors.
- Term 6. Map-matching technology: Technology to correct differences between road map information and running trajectory calculated from the measurement by self-contained navigation etc. as a measurement error, which can prevent the accumulation of measurement errors.
- Term 7. A speed sensor: A sensor to measure revolving speed of gears in a transmission to express automobile speed. All cars have this sensor.
- Term 8. Wheel speed sensors: Sensors to measure revolving speed of wheels on right and left side independently. Luxury cars have these sensors.
- Term 9. An optical fiber gyroscope: A device to measure angular velocity of rotation by emitting laser light from both ends of a rolled up optical fiber. This is based on a characteristic of lasers that the propagation velocity changes by rotation.
- Term 10. A vibration gyroscope: A device to measure Coriolis force caused by rotation of a round pillar etc. which is vibrated by piezoelectric elements. This is based on the principle that Coriolis force on a rotating object is also effective on a vibrating object.
- Term 11. VICS (Vehicle information and Communication System): A System that provides on-board car navigation systems real-time traffic information such as traffic jams, locations of road constructions and traffic restrictions. It transmits information owned by the police or road administrators by means of optical beacons or radio wave beacons set up along roads.
- Term 12. Optical beacons: Devices to transmit information of VICS to on-board car navigation systems by near infrared rays. They are set mainly on ordinary roads for car navigation.
- Term 13. Radio wave beacons: Devices to transmit information of VICS to on-board car navigation systems by radio waves. They are set mainly on expressways for car navigation.
- Term 14. ITS (Intelligent Transport System): System to transmit and receive information among persons, automobiles and roads, and solve various problems such as traffic jams, environmental problems, safety measures. Systems such as car navigation, VICS and ETC have been put into practical use up to now, and R&D on more advanced systems is ongoing for support of safe driving by inter-vehicle communication, and more efficient distribution of goods by appropriate management of the roads, etc.

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Graduated from the Graduate School of Engineering, Kyoto University in 1981. Received Ph.D. in Engineering, from Tohoku University in 2005. Joined Ministry of International Trade and Industry (MITI) in 1981. Was Director of Technology Research and Information Office, Professor at Kobe University etc. and presently Senior Analyst for Industry-Academia-Government Cooperation Promotion, METI. Working concurrently as Consulting-fellow in RIETI. Belonging to the Society for Science Policy and Research Management, Japan Society for Intellectual Production, the Academic Association for Organizational Science and Japan MOT Society. In this paper, Nomi proposed technology architecture analysis, applied it to the case of car navigation systems.



Hirosaka IKEDA

Graduated from the Department of Applied Chemistry, Faculty of Engineering, Kyushu University in 1964. Received Doctor of Engineering from Mie University in 2010. Joined Sumitomo Electric in 1964. Oversaw automotive wire harness development, vehicle electronics and NAVS. Became President at AutoNetworks Technologies, Ltd. in 1995, and Managing Director in 1999. Became Special-Appointment Professor at the Innovation Training Program Center for R&D and Business Leaders of Kyushu University in 2008, and presently Advisor at Industry-University-Government Collaboration Management Center of Kyushu University from 2014. In this paper, Ikeda was in charge of all the facts of development of car navigation systems and the way of thinking in its management.



Discussions with Reviewers

1 Overview

Comment (Naoto Kobayashi: Center for Research Strategy, Waseda University)

This paper analyzes mainly how to combine elemental technologies by studying car navigation systems whose R&D and commercialization was conducted by Sumitomo Electric, and discusses new knowledge on the methods or strategies in the new product development. The methodology to combine elemental technologies makes the basis of synthesiology, and therefore, this paper is suitable for *Synthesiology*.

Comment (Akira Kageyama: Research and Innovation Promotion Headquarters, AIST)

This paper studies the history and the method of R&D of car navigation systems as a case study, and illustrates them by re-analyzing and re-arranging them from a viewpoint of management of technology. I understood it to be an attempt to build a general method to construct technology architecture. It has been revised to a more rational and refined paper after discussions with the reviewers. Hence, this paper could be expected to diffuse its effect for improving the probability of R&D plans of new products in

companies and others.

2 Meticulousness in the logical structure

Question and comment (Akira Kageyama)

In the papers of *Synthesiology*, it is required to argue the following points, (A) and/or (B).

- (A) To describe the thinking or examining process i.e., the idea, hypothesis or discussions, by or through which a certain technology was narrowed down, when there were several candidate technologies for carrying out one function.
- (B) To describe by what thought or examination a group of elemental technologies was combined when several technologies in different technological fields were needed for achieving a certain purpose.

This paper attempts to systematize a method of how to combine element technologies in R&D of system products and presents technology architecture which uses a logical structure using symbols such as AND, OR and ADD. It is a challenging study in which Sumitomo Electric carrying out R&D and business expansion of car navigation systems is given as a concrete example. However it includes some explanations which have leaps in logic. Therefore, please reconsider those points.

Considering the history of developing car navigation systems in about 15 years from 1980s to 1990s, an argument including time axis would be necessary. In concrete terms, there were changes, for example, new technological seeds sprouted with time, and availability of new technologies for cost reduction grew by innovation or technology improvements in other industries. Logic symbol ADD introduced by the authors would be very useful for illustrating the changes of technology architecture with time. Could you show the effect of ADD more clearly?

Answer (Toshihiko Nomi)

The symbol of “↓” has been attached to the symbol “ADD” for distinguishing the base technology and the technologies added later. The new symbol “ADD↓” means that the technology written in the lower position of “↓” is added on the base technology written in the upper position of “↓,” and illustrates that a technology is added with time. Additionally, a new technology sometimes substitutes an old technology as another type of technological change with time, therefore a new symbol “OR↓” has been introduced for illustrating this type of change. This means that the technology written in the lower position of “↓” substitutes the technology written in the upper position of “↓.” By using these symbols of “ADD↓” and “OR↓,” we drew the figure of technology architecture, Fig. 14 in chapter 5, additionally, and illustrated how elemental technologies have changed in the evolution process of the car navigation systems.

In addition to the illustration of the changes of the technology architecture during the 15 years in Fig.14, we conducted a new analysis. Although in the beginning period when the performance was lower than the market needs, serious consideration was paid more to the technological performance than the cost. The cost became more important in the technology architecture after the performance for detecting current locations of vehicles was improved by the introduction of GPS. Furthermore, we showed a hypothesis that it might be useful in handling technological changes in long-term R&D management to draw a figure of technology architecture (Fig.7) containing a wide-range of substitutive technologies including candidates deemed unrealistic, and to simulate in advance how the technology architecture would change when a breakthrough occurs in a technological bottleneck.

3 Technology architecture

Question and comment (Naoto Kobayashi)

In chapter 1 “Introduction,” the authors describe that

they analyze “the way to combine elemental technologies” as “technology architecture.” Is this term used for the first time in this paper? If so, this term should be explained in detail. If the term has been already used in other papers, its source should be given clearly. This term seems to be the core concept of this paper, and is very important.

Answer (Toshihiko Nomi)

The term, “architecture,” is used frequently in system engineering etc., and recently “product architecture” or “business architecture” is used in business administration. However, “technology architecture” is a term used for the first time in this paper. Therefore, we explained the term of “architecture” and “technology architecture” in detail in chapters 1 and 2. In prior research, because the term of “architectural innovation” used by Henderson & Clark is similar to our use of the term, we explained this term in detail, and the difference between this and “technology architecture” as well.

Comment (Akira Kageyama)

Could you explain the hypothesis of the method to construct technology architecture in more detail? For example, could you do as follows:

- (1) draw a figure of technology architecture including some working hypotheses at the beginning,
- (2) clarify “AND technologies” and “OR technologies” in the above figure, and “ADD technologies” from a long-term viewpoint,
- (3) select methods to manage technologies, such as in-house development, licensing or procurement from other companies or joint-development with other companies.

By conducting these processes as one methodology, the following would become possible: ① visualizing necessary technologies, ② sharing information and a sense of value within a development project team and ③ checking validity of various decisions etc.

Answer (Toshihiko Nomi)

It would be important when considering long-term changes of technology architecture to draw a figure including unrealistic substitutive technologies with some bottlenecks as mentioned in the paper, because technological systems to be adopted sometimes change through development of unexpected new technologies or changes of social conditions.

And, because there are various paths connecting elemental technologies and a product, a selected course sometimes changes in response to the progress of elemental technologies. A figure of technology architecture is expected to serve as a map to overview the whole including various courses. This would be useful for examining technological paths or technology road maps to improve performance or functions of a product through its generational changes.

Additionally, technology architectural figure including a wide range of substitutive technologies would be useful for considering impacts, i.e. risks and chances for the businesses by the development of new technologies in the future. Managers and researchers/engineers could hold discussions, and examine business strategies and R&D strategies integrally by using this figure.

4 Possibility for future development or research

Comment (Akira Kageyama)

Although this paper points out the advantage for prior consideration of an R&D plan at the end of chapter 5, could you show “some examples as hypotheses”? Two or three examples to which figures of technology architecture are applicable would make readers understand this analysis better, and motivate them to draw such a figure, even if the examples are not so detailed as

in the case of car navigation systems.

Answer (Toshihiko Nomi)

Car navigation systems analyzed in this paper are about to be developed further toward intelligent transportation systems (ITS), therefore the technology architecture analysis would also be useful for examining the R&D plan of ITS, for example, examining what functions the total systems should have, or what elemental technologies should be developed for those functions. Moreover, as there is an increasing trend to use robots in daily life such as in nursing care, or in the field of agriculture, forestry and fishing, the technology architecture analysis would be useful for examining the R&D plans of robots, such as examining what functions robots should have, what technological issues should be derived from the breakdown of those functions, or what technological seeds would be needed. Therefore, we added these examples at the end of chapter 6.

5 Generational changes in car navigation systems

Comment (Naoto Kobayashi)

There are explanations that the first generation of car navigation systems has the function “to detect current locations,” the second generation the function “to route guide to destinations” and the third generation the function “to route guide by taking into account additional information.” Please inform us whether the researchers made the initial R&D plan with an awareness of these generations, or whether characteristics of generations emerged as a result of the changes of the development goals according to the technology advancement and changes of the market needs.

Answer (Hirosaka Ikeda)

Sumitomo Electric was aware of possible future development up to the “third generation of car navigation systems” from the beginning of the R&D of car navigation systems, and it proceeded with the development. Because the usefulness of a car navigation system “was proven in guiding vehicles to uncrowded roads using traffic information” by a test in a large-scale R&D project the “Comprehensive Automobile Traffic Control System” started in 1973 as mentioned in reference [13], the company set the goal to put this system into practical use.

For this purpose, it proceeded with the necessary development of car navigation systems, elemental technologies and social systems simultaneously, and realized them according to the time order of steps 1, 2 and 3 according to the order of possibility for commercialization. Actually, the company approached the National Police Agency, the Ministry of Construction, and the Ministry of Post and Telecommunication, which resulted in the establishment of the Japan Digital Road Map Association and the Vehicle information and Communication Systems Center, and traffic information began to be distributed. Although Sumitomo Electric made efforts to develop such social infrastructures for car navigation systems, it could not reflect its efforts to its business.

This was one of the reasons for its withdrawal from the car navigation business.

6 Future development of the world market of car navigation systems

Comment (Naoto Kobayashi)

Although Japan had about 100 % of the share in the world market of car navigation systems in 2004, its share dropped steeply to 20 % in 2007. One reason is said to be because portable navigation devices (PND) whose prices were overwhelming low diffused, and grabbed the market share of Japanese companies which were producing high-performance and high-price types of products installed in cars. This means that cost (price) was selected in the choice of performance and cost. On the other hand, there is another possibility that car navigation systems would be upgraded more and more in the future equipped with many sensing and acting functions for automatic driving systems of cars. Please show the global strategy of Japanese companies for car navigation systems of the future, if possible.

Answer (Toshihiko Nomi)

It is said that there is a trend for bipolarization of high-performance products installed in cars and low-cost portable navigation devices (PNDs) in the market of car navigation systems. Although car navigation systems which showed the current vehicle location on a road map didn't exist in the market other than Japan in the past, a low-cost portable navigation device (PND) developed by a Dutch company diffused explosively in the European and the U.S. markets, and then expanded its sales rapidly in the Chinese market. For that reason, Japanese companies dropped their global share in unit sales. However, this did not mean the decrease of sales of Japanese companies. Many Japanese companies have entered into the PND business in the Japanese market. On the other hand, car navigation systems installed in cars have advanced toward high-performance by introducing voice recognition technology, an on-board camera and a head up display, to say nothing of integration with a car audio. In addition, it is said that the sales number of PNDs in the global market decreased in 2011 because the function of navigation was added to smart phones. Recently, the issue is the choice between low-price products which only show navigation information from a connected smart phone on a display and high-price products installed in cars.

Additionally, car makers are examining strategies, such as to use big data by connecting a car navigation system with the Internet, or to realize automatic driving by using the route guide function of a car navigation system. It is also said that Google intends to develop automatic driving technology, and to get its de facto standard. In the advance of car navigation systems, various industries and various companies are contemplating their own strategies, and the future course of events is very fluid.

Clean and practical oxidation using hydrogen peroxide

— Development of catalysis and application to fine chemicals —

Yoshihiro KON, Shinji TANAKA and Kazuhiko SATO *

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Oxidation is an important component in over 30 % of chemical processes. However, oxidation typically creates environmentally damaging waste products. Hydrogen peroxide (H_2O_2) is a good candidate for environmentally benign oxidation because the only by-product is water. By integrating key technologies for halogen-free, organic solvent-free processes, and designing suitable metal catalysts, we succeeded in the development of H_2O_2 oxidation. This achievement is the first concrete example of Green Sustainable Chemistry (GSC). Based on this new technology, we further attempted to establish H_2O_2 oxidation as a practical method for the formation of fine chemicals of high performance. Novel catalysts optimized for practical usage were developed by resolving key issues such as cost reduction and scalability through joint research between AIST and various chemical companies.

Keywords : Green sustainable chemistry, oxidation, hydrogen peroxide, catalysis, fine chemicals

1 Introduction

Chemical products are contained in various products around us including automobiles, home appliances, office appliances, clothes, and drugs. Our lives will be set back without chemical products. The chemical industry is an important key industry for Japan, and Japan is one of the primary chemical product producers in the world.^[1] Although oxidation reaction is the most important reaction that dominates over 30 % of all chemical processes, it is also known as a process that severely contaminates the environment, as large amounts of waste derived from oxidants are produced as by-products of the reaction.^[2] Table 1 summarizes the major oxidants, waste products after the reaction, percentage of active oxygen, and appropriateness as clean oxidants. Nitric acid (HNO_3) is an oxidant used in the production of adipic acid that is used as the raw material of chemical fibers, and water (H_2O) and nitrous oxide (N_2O) are produced after the reaction. Nitrous oxide is known as a greenhouse gas, and it is calculated that 2.2 million ton/year of adipic acid is produced worldwide, and 400 thousand ton/year of nitrous oxide is produced as waste. Sodium hypochlorite (NaClO) and paracetic acid (CH_3COOOH) are used in the production of electronic materials and drugs, and compounds containing chlorides (NaCl) and acetic acid (CH_3COOH) are produced in amounts greater than the target product after reaction.^[3] These waste products severely contaminate the environment and cannot be released directly into the air, river, or ground, and therefore, the manufacturers must design a process where the waste derived from the oxidants are collected, recycled, and reused. However, considering the construction of facilities that do not leak waste products, energy needed for

processing, and efforts to reduce exposure during work and safety maintenance, the load on the environment is extremely high. For a fundamental solution, it is necessary to use an environmentally benign oxidant from the beginning. Oxygen (O_2) is ideal as an oxidant with low environmental load, but using both of the oxygen atoms in O_2 in the oxidation reaction is an unknown reaction in actual science although it may be discussed in theory. Even if a reaction system is designed where one of the oxygen atoms is used in oxidation while the other atom is emitted as water, it is difficult to have only the target reaction to progress or to control it, and there is the disadvantage that the oxidation may progress all the way to carbon dioxide (CO_2) past the target chemical product.

We looked at hydrogen peroxide (H_2O_2) as a clean oxidant. Hydrogen peroxide is a colorless, transparent liquid discovered by a French chemist, Thénard in 1818. Currently, the solution with concentration of 60 % or less is available as an industrial product. The domestic shipment of hydrogen peroxide has been stable at about 180~200 thousand ton/year for the past few years,^[4] and it is used widely in our daily lives. For example, it is known at home as liquid bleach detergent or disinfectant oxydol. In industrial use, it is used for bleaching paper and pulp, wastewater treatment, soil improvement, or semiconductor cleansing. The structure is a combination of two each of hydrogen (H) and oxygen (O) in the form of H-O-O-H, and it has equivalent percentage of active oxygen as oxygen (47 %) and the waste is water only. Until now, hydrazine, catechol, oxime, and propylene oxide manufacturing have been industrialized, and it is expected that chemical product synthesis using hydrogen peroxide will increase in the future (Fig. 1). However, the oxidative

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Table 1. Comparison of various manufacturing methods

| Oxidant or manufacturing method | Waste product | Percentage of active oxygen (%) | Appropriateness as clean oxidant and remarks |
|--|--|---------------------------------|--|
| Oxygen (O ₂) | None | 100 | ◎(Difficult to control, catalyst required) |
| Oxygen (O ₂) | Water (H ₂ O) | 50 | ○(Difficult to control, catalyst required) |
| Hydrogen peroxide (H ₂ O ₂) | Water (H ₂ O) | 47 | ○(Catalyst required) |
| Nitric acid (2HNO ₃) | Water + nitrous oxide (N ₂ O) | 51 | △(Emit greenhouse gas) |
| Sodium hypochlorite (NaClO) | Sodium chloride (NaCl) etc. | 22 | ×(Emit chlorine compounds) |
| Peracetic acid (CH ₃ COOOH) | Acetic acid (CH ₃ COOH) | 18 | ×(Produce acetic acid) |

◎: Optimal, ○: Appropriate, △: Treatment necessary, ×: Inapplicable

capacity of hydrogen peroxide itself is low, and activation by optimized catalysts is necessary for its application to various chemical reactions. For hydrogen peroxide to be used widely and generally as a clean oxidant, it is necessary to develop not only the basic chemical products, but also the core technology for new catalysts that allow application to fine chemicals, electronic materials, and drug manufacturing.

2 Background of the development of environmentally benign hydrogen peroxide oxidation technology

Here, we describe the steps that lead to the start of the development of our hydrogen peroxide oxidation technology against a background of green sustainable chemistry. The social trends in industry and environment are shown on the left side of Fig. 2 while the technological trends of hydrogen peroxide oxidation are shown on the right side. As shown on the left side of Fig. 2, environmental pollution was recognized from the latter half of the 19th century. From the 1950s to 1980s, the issue of environmental pollution such as air, water, and soil became serious due to the development of various chemical product manufacturing processes, and the industries were obliged to reduce and process the waste before release. In the 1990s, the movement to conserve the environment became active internationally. In 1991, Paul Anastas stated the 12 principles of green chemistry,^[5] and in 1997, Kyoto Protocol that stated the reduction target for carbon dioxide

for each country was adopted. Active discussions were engaged internationally on the environmentally friendly manufacturing method for chemical products, and the direction of constructing environmentally benign chemical processes was indicated as part of the solution. On the other hand, a specific guideline for what kind of technology should be developed to realize an environmentally benign chemical process had not been discerned at this point. Next, looking at the right side of Fig. 2, the oxidation technology for hydrogen peroxide was developed at about the same time when the environmental conservation movement became active. The publications on activating hydrogen peroxide using catalysts were seen from around 1950, and in the 1980s, catalyst technologies with high selectivity or high applicability for actively synthesizing target compounds were published abundantly. For example, in 1983, Venturello *et al.* reported the hydrogen peroxide oxidation reaction using a catalyst containing tungsten acid, and in 1988, Ishii *et al.* reported the hydrogen peroxide oxidation reaction consisting of two components, tungstophosphoric acid and quaternary ammonium salt.^{[6]-[8]} However, although such catalytic reaction implied clean reaction using hydrogen peroxide, it did not actively promote a practical, environmentally benign method, and used halogen compounds and organic solvents to enhance the catalytic activity. It is insufficient

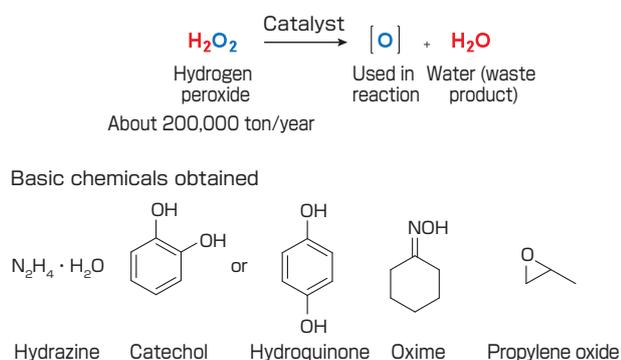


Fig. 1 Hydrogen peroxide oxidation technology in the manufacturing of basic chemical products

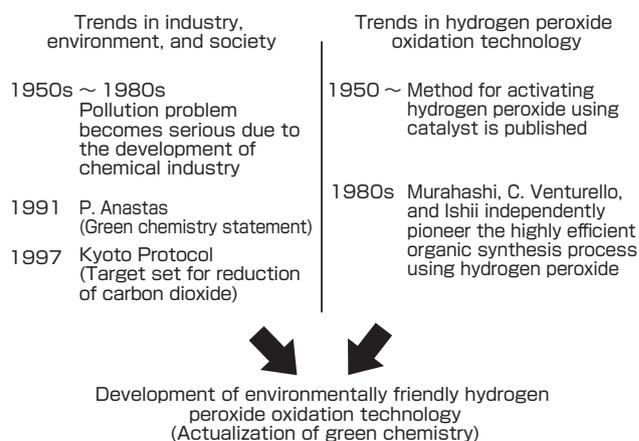


Fig. 2 History of the development of environmentally friendly hydrogen peroxide oxidation technology

to simply use hydrogen peroxide to achieve a sustainable chemical reaction, and it must be clean for the entire process from the raw material stage, manufacturing, refining, through to cleansing. With this way of thinking, we set the objective to conducting the hydrogen peroxide oxidation in an environmentally benign manner. We thought we could achieve an effective environmentally benign process if we could manufacture specific catalysts that can synthesize target products with high yield and high selectivity under the conditions of halogen free and organic solvent free, and started the development of the basic technology for oxidation process including the catalyst development.

3 Development of a new catalyst that enables environmentally benign hydrogen peroxide oxidation technology

Under Professor Ryoji Noyori, who is world renowned for reduction reaction, we engaged in the development of oxidation reaction, and after a five-year period of trial-and-error during which we were unable to publish papers or make presentations at academic societies, we developed a new catalyst. The specific flow of research was: set a working hypothesis → verify the hypothesis through experiment → extract problems through examination → set a working hypothesis again. This was repeated until we discovered a catalyst that allowed us to obtain the target substance at high yield. By repeating the trials-and-errors and reviews over several hundred experiments, the key point of the oxidation by hydrogen peroxide became clear, and we extracted the following elemental technologies: (1) halogen-free technology, (2) organic-solvent-free technology, and (3) metal catalyst design technology. By conducting the catalyst design repeatedly to avoid the decrease of reactivity that may occur due to the combination of various elemental technologies, we were able to discover the true active species of the reaction, and succeeded in developing a sustainable hydrogen peroxide oxidation technology.^[9] For catalyst development, the technological development up to this point is reconsidered from the perspective of the integration of elemental technologies, and we propose it as one of the guidelines for a highly efficient way of developing a new catalyst.

3.1 Design of a tungsten catalyst based on conventional knowledge

On the hydrogen peroxide oxidation technology as described in chapter 2, the basic research for the activation of hydrogen peroxide by catalysts became active from the 1950s. From the findings so far, it is known that the efficiency of hydrogen peroxide increases when tungsten is used as a catalyst, since it does not decompose hydrogen peroxide. For the structure of the active species, according to the prior research by Venturello *et al.*, the binuclear or tetranuclear complexes were proposed, with a triangle composed of tungsten and two oxygen atoms as the basic unit (Fig. 3, Catalyst A).^[10]

Moreover, since the hydrogen peroxide oxidation reaction is a two-phase reaction between the organic phase (raw material) and the liquid phase (hydrogen peroxide), simple mixing does not bind them, and it is known that the use of quaternary ammonium salt, which is a type of a phase transfer catalyst, is necessary to efficiently promote the reaction. Utilizing the findings from the prior research, we decided to develop the catalyst based on the combination of the tungsten metal catalyst and the phase transfer catalyst.

3.2 Reaction mechanism of the tungsten catalyst and the effect of a halogen solvent in the conventional method

There were two problems in the conventional method: the use of organic solvents such as a halogen solvent and the use of halogenated quaternary ammonium salt. However, at the time, it was common knowledge that the halogen solvent was necessary to increase the efficiency and selectivity of the reaction in hydrogen peroxide oxidation technology.^[11] The reason will be explained alongside the description of the reaction mechanism. Quaternary ammonium salt becomes stable as it is in neutral condition by becoming cation and anion species. The tungsten catalyst also forms salt with the sodium cation, after forming active anion species by directly bonding with hydrogen peroxide (Fig. 3, Catalyst A). Then through the cation species exchange from sodium cation to quaternary ammonium cation, the active anion species is transferred to the organic phase using the power of quaternary ammonium salt that readily dissolves in the organic phase (Catalyst B). After the reaction in the organic phase, the salt of tungsten anion species with one less oxygen atom and the quaternary ammonium cation (Catalyst C) return to the liquid phase along with the sodium cation that readily dissolves in water, through the exchange from the quaternary ammonium cation to sodium cation (Catalyst D). Then, it comes in contact with hydrogen peroxide to recreate the active anion species (Catalyst A). The cycle of Catalyst A → B → C → D is repeated as the reaction progresses. To promote the reaction efficiently, smooth transfer from

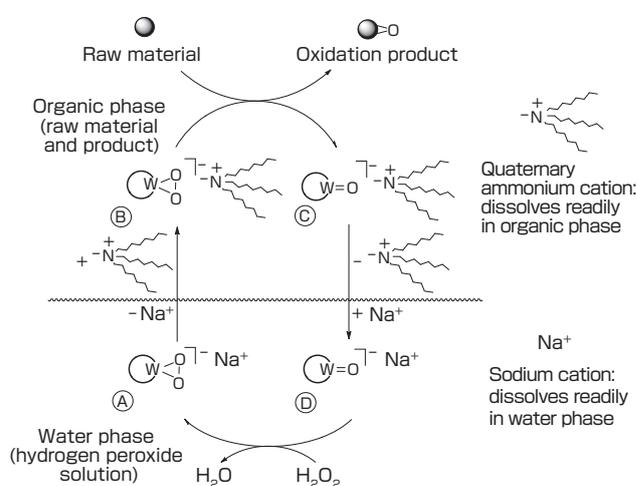


Fig. 3 Reaction mechanism of the hydrogen peroxide oxidation technology using tungsten catalyst

water to the organic phase (transfer from Catalyst A to B) is considered most important. Since the halogen solvent has particularly high affinity with quaternary ammonium salt among the organic solvents, it is said to be the optimal solvent for the transfer from water to the organic phase. Also, since the halogen solvent does not readily mix with water, the reaction phase (organic phase) and the catalyst-activating phase (water phase) do not undergo mutual mixing, and the individual routes from Catalyst B to C and Catalyst D to A progress highly efficiently.^[12] However, since the top priority objective of this research was the development of an environmentally benign process, we could not use any of the organic solvents including the halogen solvent. It was necessary to develop a highly efficient, new catalyst that greatly surpassed the disadvantage of using no organic solvents including halogen.

3.3 Development of the halogen-free and organic solvent-free tungsten catalyst technology

In the oxidation reaction from 2-octanol to 2-octanone, when only the organic solvents were removed using the conventional tungsten catalyst, the yield dropped from 90 % to 11 % and the reaction almost ceased to progress. While it involved simply removing the organic solvents, for organic synthesis in which the core technology was the optimal selection of the organic solvents, the reaction system where organic solvent could not be used was a system where the conventional knowledge was totally useless, and new concepts had to be pioneered. As a solution, we made a main assumption that the reaction will not occur unless the raw material and the active species came into contact, and investigated the improvement of the phase transfer catalyst that greatly affected the contact. Quaternary ammonium salt used for the phase transfer catalyst is composed of an ion pair of quaternary ammonium cation and chloride ion (anion species), and as shown in the reaction mechanism (Fig. 3), the quaternary ammonium cation pairs with the tungsten active species to become actively involved in the reaction, while chloride ion is not directly involved in the reaction mechanism. We first considered the improvement of the quaternary ammonium cation, but were unable to see hardly any increase in reactivity when the affinity to the organic solvent was enhanced by lengthening the alkyl chain two or three times longer. Next, we looked at chloride ions. As it did not appear in the reaction mechanism, it was thought that the change in chloride ion seemed to have no effect on reactivity, we decided to actively search for halogen-free anion species to replace the chloride ion to achieve environmental

benignity for this technological development.

As we engaged in the experiments and reexaminations on the effects of the anion species, we learned that there was a possibility that the anion species actively affected the structure of the active species. That is, we found that the tungsten active species took on three structure types according to the strength of acidity (pH) of the water phase. Among the three, Type A2 had the highest reactivity, and this structure was present in pH 0.4-3.0 (Fig. 4). Based on the assumption that the reaction will progress extremely efficiently if the pH during the reaction could be maintained between 0.4 to 3, we investigated the effect of the anion species in the oxidation reaction of 2-octanol. We obtained the result that while the yield was 11 % in the case of chloride ion, the yield increased to 97 % when hydrogen sulfate ion was used, and the change of anion species clearly improved the reactivity. When the pH during the reaction were measured for chloride ion and hydrogen sulfate ion, the pH changed to 4 or more immediately after the start of the reaction for chloride ion while the pH stayed at an ideal condition of 2 to 3 in the case of hydrogen sulfate ion.

The examination of the anion species of quaternary ammonium salt that was started to establish the halogen-free, organic solvent-free technology led to the detailed clarification of the true active species of the tungsten catalyst, as a result. When conducting catalyst design, without changing the goals and conditions that were set initially, one can find a solution by accurately evaluating the experimental results, seeking the essential principle that lies deep down, and thoroughly understanding the reaction in accordance to the basic principle, even if the experimental results are not good. In this case, we set the elemental technologies for organic solvent-free and halogen-free processes, did not change them during the course of research, continued the search for the catalyst, and then, we became aware of the change of the structure of tungsten active species according to pH. Therefore, we reached a deep understanding of the tungsten active species and were able to develop a highly active catalyst unseen before.

3.4 Review of the working hypothesis to apply the developed catalyst to epoxidation reaction

The activity of the developed catalyst was extremely high, and it enabled the oxidation of various alcohols and the highly efficient synthesis from cyclohexene to adipic acid.^[13-15] When the turnover number of the catalyst (how many raw materials

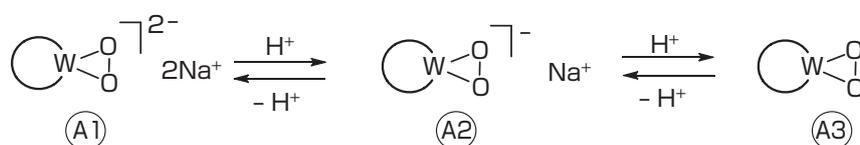


Fig. 4 Three forms of tungsten catalyst active species A according to pH

are oxidized by one catalyst) that is the index of catalytic activity was investigated, the number surpassed 70 thousand times, and this indicated that the catalytic activity was two digits higher than the conventional method using the halogen solvent. However, when epoxidation was attempted using this catalyst, unlike alcohol, extremely low reactivity of 5 % yield was seen in the reaction of 1-octene. Therefore, we improved the developed catalyst to be applicable to epoxidation. Since the route from active species A to B shown in Fig. 3 was optimized, we thought the reason for the slow reaction progress was in some other steps. As a result of investigation by various experiments, it was found that the oxygen of active species B was not readily attacked by the olefin moiety of the raw material. We redesigned the catalyst that combined phosphorus and nitrogen to the binuclear complex structure of tungsten so the oxygen of active species B would readily come in contact with the raw material (Fig. 5). That is, by adding the aminomethylphosphonic acid as a “reaction site activating catalyst,” one of the catalyst component, a hydrogen bond formed between N-H and O-W, oxygen in W-O of the reaction side decreased the electric charge, and it would be readily attacked by the olefin. When the reaction was actually conducted by adding the aminomethylphosphonic acid in the oxidation of 1-octene, the reactivity dramatically increased even though only one component of the catalyst was added, and epoxides were given in 94 % yield.

3.5 Point of catalyst development

We succeeded in developing an environmentally benign oxidation technology that was halogen-free and organic solvent-free, through the combination of quaternary ammonium salt of hydrogen sulfate and aminomethylphosphonic acid, using a tungsten catalyst as the base. Without being bound by conventional way of thinking that halogen solvents were absolutely necessary or quaternary ammonium salt anion species were not involved in the reaction, we reached the true core of the reaction. We were able to develop a highly efficient catalyst through a strategy of thoroughly removing the uncertain factors by making minimal changes to the catalyst design to solve the problem and then to continue improving the catalyst. The developed technology led to the first paper in the world to specifically present which organic synthesis

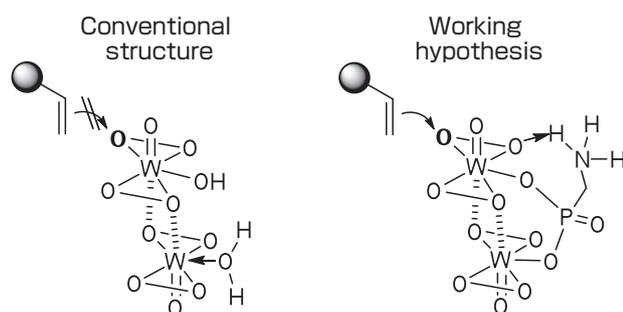


Fig. 5 Working hypothesis for the tungsten catalyst active species for epoxidation

was effective for reducing the environmental load, in the green sustainable chemistry field that merely stated theories, and created a new trend in the research of green sustainable chemistry.

4 Practical application of the adipic acid synthesis method for use in core technology

Although there are many kinds of chemical products, we looked at the adipic acid that is known as the raw material for 6,6-nylon that is necessary for chemical fibers, interior decorations, and automotive parts. Most of the industrial manufacturing method that are currently in operation are conducted by the nitric acid oxidation of cyclohexanol and cyclohexanone derived from benzene (Fig. 6). In nitric acid oxidation, nitrous oxide is produced as a co-product, and we thought that the merit of replacing it with hydrogen peroxide was great. Using the 30 % hydrogen peroxide solution as an oxidant and the tungsten catalyst system developed in subchapter 3.4,^{[13][14]} we started joint research with companies for commercial industrialization. In industrial use, the points of not using organic solvents and reusing the catalysts were major advantages. However, cost was a problem. For the use of raw materials and catalysts, the raw materials were the same and the amount of catalyst used was small, and this did not greatly affect the cost. On the other hand, in the existing manufacturing method, the oxidant used was nitric acid that is less expensive than hydrogen peroxide. Since it became apparent that the newly considered process will incur higher cost compared to the conventional method due to the cost of oxidants, and there was additional expenditure to build a new plant, commercialization was not realized.

5 Elemental technologies that must be considered in realization research and setting of the integration system

The failure with adipic acid indicated that it is necessary to consider various factors such as cost and scaleup as well as the catalyst technology to achieve realization. Reflecting on

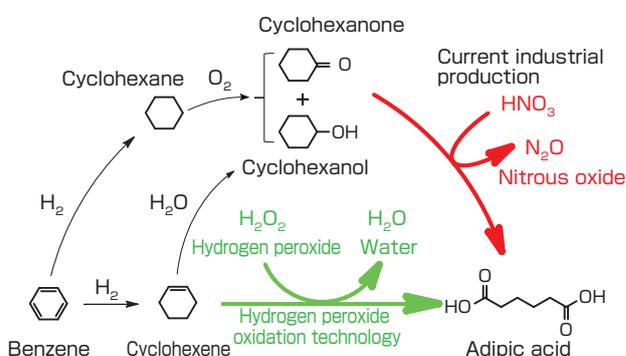


Fig. 6 Comparison of the conventional method and the manufacturing of adipic acid using hydrogen peroxide oxidation technology

these points, we set the milestones or elemental technologies that must be considered in the realization research (Fig. 7). Solving these elemental technologies individually means that the realization research will progress as the issues are cleared one by one while integrating the elemental technologies.

Although the core of our research is the creation of a new catalyst that may use hydrogen peroxide as an oxidant, simply creating a catalyst does not lead to practical use, and the selection of the target compound, scaleup, and investigation and research on cost estimates are essential. To promote such investigation and research, joint research with companies is mandatory, and the road to practical use will open through close collaboration with the parties involved. In the following sections, the importance of individual elemental technologies is considered taking the example of adipic acid, and the guideline for promoting realization research is presented.

5.1 Selection of the target compound

The product manufactured must not be the result of a mere replacement of a manufacturing method. It will not have market competitiveness unless it has strength or performance

that far surpasses the conventional product. The replacement of the manufacturing process for which the method has matured and has a long history of operation is difficult unless the newly developed technology shows improvement and merit that further surpass the conventional technology. For example, adipic acid has been produced stably for several decades using the nitric acid oxidation method. The system to completely recover the emitted nitrous oxide and to convert it to nitric acid without much loss has been well established. Since the conventional method is mature, the possibility of employment of any new method is extremely low.

Moreover, in selecting the target compound as part of the environmental-load-reducing technology, it is necessary to consider the E-factor. Figure 8 shows the correlation of the manufactured amount of chemical products and the E-factor. The E-factor is the amount of waste produced when manufacturing one kilogram of a target product, and ideally, this value should be 0. As shown in Fig. 8, the E-factor becomes large in the manufacture of products with high added value because the manufacturing process becomes complex and multi-stepped.^{[16][17]} Drugs and electronic materials have

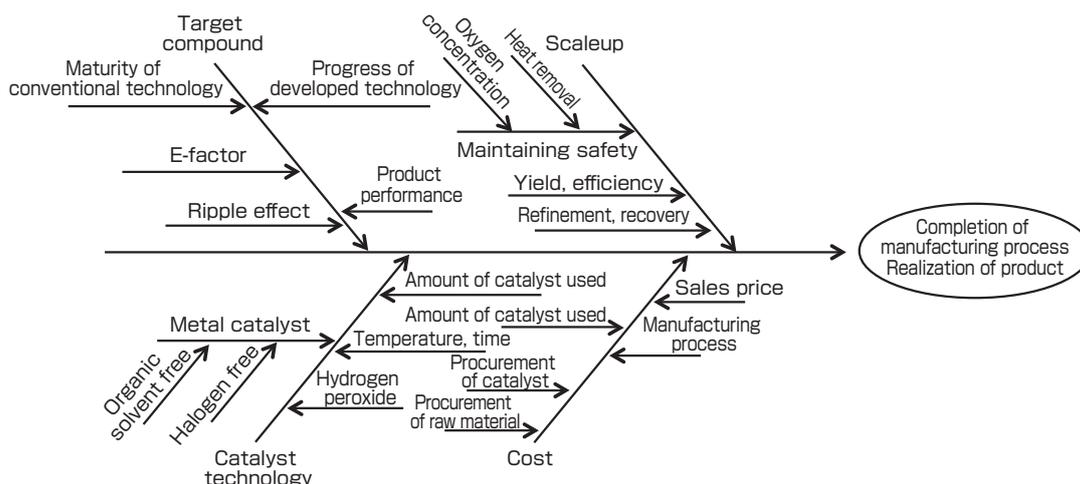


Fig. 7 Milestones that must be considered in realization research

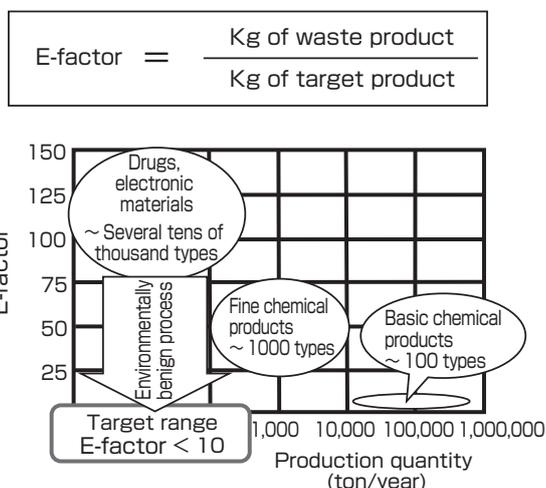


Fig. 8 E-factor in chemical industry

higher market prices compared to basic chemical products, and the size of their E-factors have been overlooked since profit can be made even though the cost of processing the waste is high. As a result, as there are many types of drug and electronic materials, even though the production volume per type is small, the total amount of waste generated amounts to more than half of the entire petrochemical industry.^[2] Therefore, to convert the manufacturing method of the so-called functional chemicals including the intermediate and raw materials of the drugs and electronic materials that have large E-factors or large waste volumes to a method that is environmentally friendly will dramatically reduce the E-factor, and also reduce the total amount (or absolute amount) of waste. Since the adipic acid is a basic chemical product and the process is matured, the E-factor is basically low. If the target compound is selected according to the E-factor, the significance will be great if the manufacturing method of the so-called functional chemicals, such as the intermediate and raw materials of drugs and electronic materials that has E-factors that reach 100 to 150 and produce high volume of waste, can be changed to a method with E-factors of 10 or less.

In selecting the target compound, it is extremely important to consider the ripple effect and additional value. Since much labor and time is necessary for the development and realization of a new technology, it is essential during the R&D process to select a target compound assuming that the obtained new technology can be used for the manufacture of similar products or the produced materials can capture high percentage of share among materials due to its high performance. In the future, the demand will be high for a manufacturing method that is environmentally benign and also has high performance, not simply replacing the conventional technology with one that is environmentally benign. As it will be described later, the halogen-free technology has the potential to dramatically increase the performance of the electronic materials and therefore to create new values, and it can be a powerful elemental technology.

5.2 Catalyst technology

For catalyst technology, only the outline will be presented as the details are explained in chapter 3. We possess highly efficient, highly selective oxidation technology through the design of new catalysts based on metal catalysts under the condition of not using organic solvents and halogen and using hydrogen peroxide as the oxidant. The technology developed surpasses the existing catalysts in turnover number and has low environmental load. Specifically, it uses two component catalysts composed of tungsten and ammonium salt for the manufacture of alcohol and adipic acid, and also uses three component catalysts combining a single reaction site activating catalyst for epoxidation. To complete the catalyst technology as a process, it is also necessary to optimize the reaction time and temperature, adjust the adding method of raw materials or catalysts, and minimize the amount of catalysts

used. Moreover, our technology is the basic technology of hydrogen peroxide oxidation and can be applied to various raw materials, but highly efficient reaction cannot be achieved even if the publicized technology is used directly for target reaction. Depending on the target reaction or structure of the raw material, the optimal catalysts are different. Therefore, it is necessary to pinpoint the metal catalyst, the phase transfer catalyst, or the reaction site activating catalyst that are specific to the manufacture of the desired target product, although the basic technological concept of the three-component catalyst system composed of tungsten acid, quaternary ammonium salt, and phosphorus compound is used. In doing so, a quick discovery of the optimal catalyst for the manufacture of a target product is only possible in the presence of the ability to select and discard the factors with maximum effect for promoting the reaction, through clarifying the reaction mechanism from the basic principle, backed by the knowledge and experiences that were obtained through the development of the basic technology for hydrogen peroxide oxidation. That is, in shortening the development period or gaining the economic competitive edge, it is necessary to maintain and deepen the platform of findings on the reaction mechanism and basic principles that were obtained through the development of the basic technology for catalysts, and to utilize them for the invention and discovery of the optimal catalyst system to synthesize the target product.

5.3 Cost

In considering the cost, joint research with companies is mandatory. To develop the technology by which one can claim that the environmentally benign method has clear cost advantage, through objective comparison of the conventional and new methods of manufacturing process, is essential for realizing environmentally benign oxidation technology using hydrogen peroxide. As a specific example, the cost comparison of the manufacture of adipic acid and epoxides, the raw material of the insulating film (explained later), is presented (Fig. 9). In the case of the adipic acid, the price difference of the oxidant is directly reflected in the cost because it does not have high added value as a product, although it can be produced in vast amounts. It is difficult to apply the hydrogen peroxide oxidation technology to the manufacture of chemicals with low price due to the cost of the oxidants. On the other hand, in the manufacture of epoxides for functional chemicals with relatively high price, although the difficulty of the manufacturing technology may increase, the merit of manufacturing using the hydrogen peroxide oxidation technology is obtained by developing the catalyst technology and scale-up technology (new methods are described in chapter 6). In reality, the calculation results shown here do not necessarily reflect the actual situation at the manufacturing plant, and the figures may be wrong in many cases. However, in conducting the realization research and engaging in joint research with the companies, it is necessary to exclude subjects that clearly do not match the price, and to recognize to some

degree the difference between the actual cost of the subjects that one wishes to pursue and the target values at a level that can be realized, at the start of the realization research.

5.4 Scaleup

In terms of extracting the problems in manufacturing, the consideration of scaleup is necessary. It is known that in the hydrogen peroxide oxidation technology, oxygen is produced through the decomposition of hydrogen peroxide. To check the safety during manufacturing, it is necessary to monitor the oxygen concentration during reaction, check the heat generation of the reaction vessel, and to take measures to keep it under the specified value. The hydrogen peroxide oxidation technology we developed is done in a batch reaction vessel where the raw materials, catalysts, and hydrogen peroxide solutions are all placed in one vessel and then mixed, and in scaleup, the issues of the removal of the reaction heat produced and the reduction of the reaction site due to decreased interface between the organic and water phases cannot be avoided. It is necessary to investigate the effects of such negative factors on the yield and the reaction speed, and it may become necessary to redesign the catalyst in some cases. Also, to stably manufacture a product in designated amounts, it is also necessary to consider the refining process and the recovery and reuse of catalysts.

6 Manufacture of the ultra-long life insulation film using the hydrogen peroxide epoxidation technology

6.1 Setting of the target compound

The development of alicyclic epoxide manufacturing process using hydrogen peroxide oxidation useful for insulation materials was conducted jointly with Showa Denko K.K.^{[18]-[20]} The insulation materials are used in all sorts of electronic parts from large liquid crystal displays to cell phones. In the liquid crystal panel, the control board is made by directly installing the chip on the film substrate used for wiring, and the epoxy resin that can be readily painted on and hardened is used as the insulating material to cover the fine wires (Fig. 10). The pursuit of high functions and weight reduction of the electronic parts will continue further in the future, and the achievement of flexibility of the printed substrate and fine wiring (further narrowing of the pitch) are necessary technologies. Moreover, higher insulation performance and flexibility compared to the conventional materials are demanded for the materials that cover and protect the circuits. In the conventional manufacturing technology, the use of chloride compounds is necessary, and there are problems of not only producing large amounts of chloride waste, but the minute amount of organic chloride compounds remaining in the product may short-

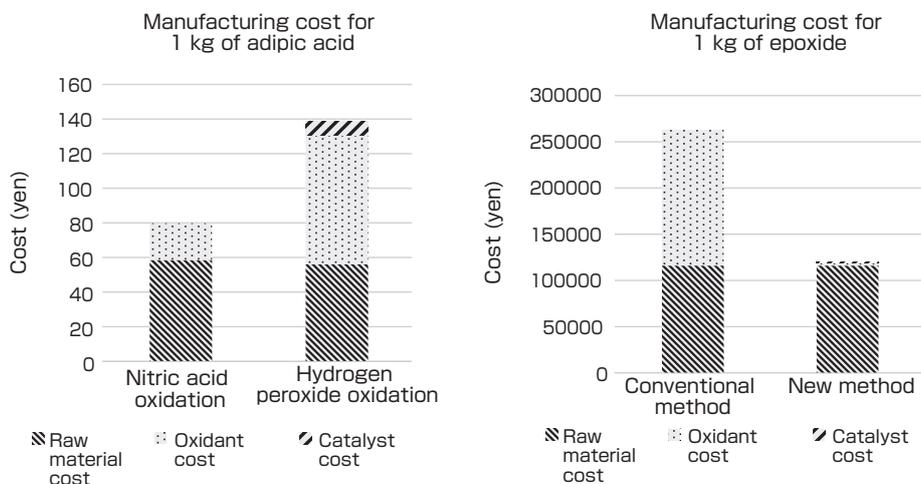


Fig. 9 Comparison of the manufacturing cost

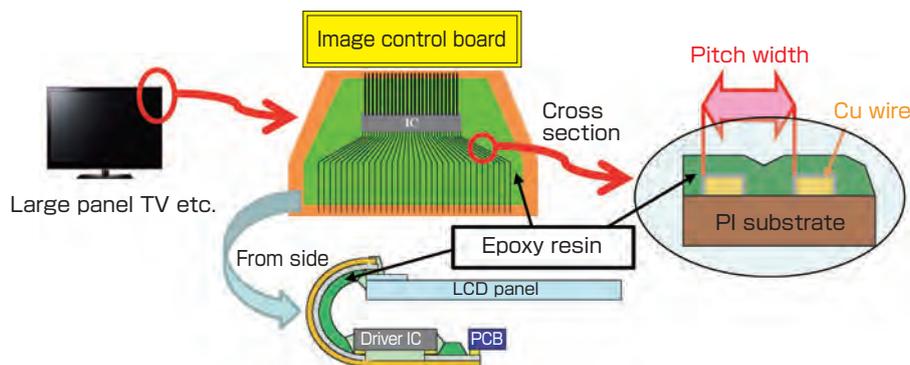


Fig. 10 Development of the epoxy resin for electronic material

circuit the fine wires and damage the long-term insulation property. We developed technology for hydrogen peroxide oxidation using new catalysts to manufacture epoxides while satisfying the above performances.

6.2 Catalyst development, cost reduction, and scaleup

We developed the catalyst considering the properties of epoxides based on our basic technology for hydrogen peroxide catalysts. We investigated the scaleup and cost. Ultimately, to meet the demands of the user companies, we achieved 10 times catalyst use efficiency by optimizing the catalyst reuse technology and the method of adding hydrogen peroxide, and reduced the cost of catalysts to one-tenth of the initial target value (Fig. 9). By devising the reaction vessel and mixing method as well as strict control of reaction temperature, we succeeded in developing a chloride-free selective epoxidation

technology at 20 kg scale (71 % yield, 90 % selectivity). Since this step is an optimization of the process specific to the target chemical product and manufacturing equipment, although much time and labor are spent, the obtained findings cannot be written up as papers or patents. However, we felt that by achieving the target values of manufacturing process through working with the companies, we actually saw the possibility of realization of our developed technology.^[21]

6.3 Fabrication and evaluation of the insulation film

By oligomerizing the obtained epoxide and combining with a hardener, we completed the ultra-long life insulation film (Fig. 11). To evaluate the performance as an insulation film, we conducted the test of insulating durability at high temperature and high humidity (85 °C, 85 % Rh). As shown in Fig. 12, the conventional product short-circuited and the

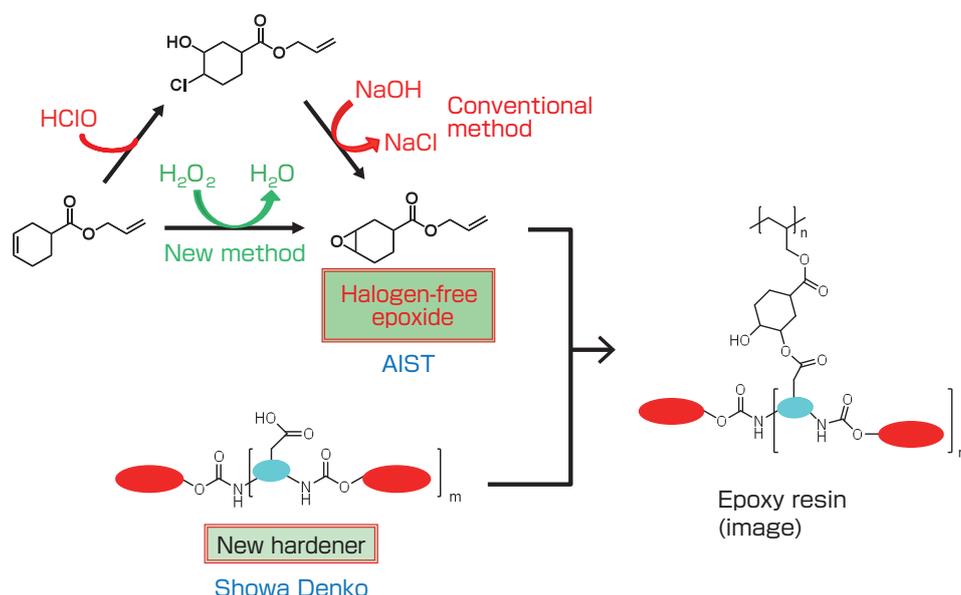


Fig. 11 Development of the oxidation technology using hydrogen peroxide and the manufacture of fabricated epoxy resin

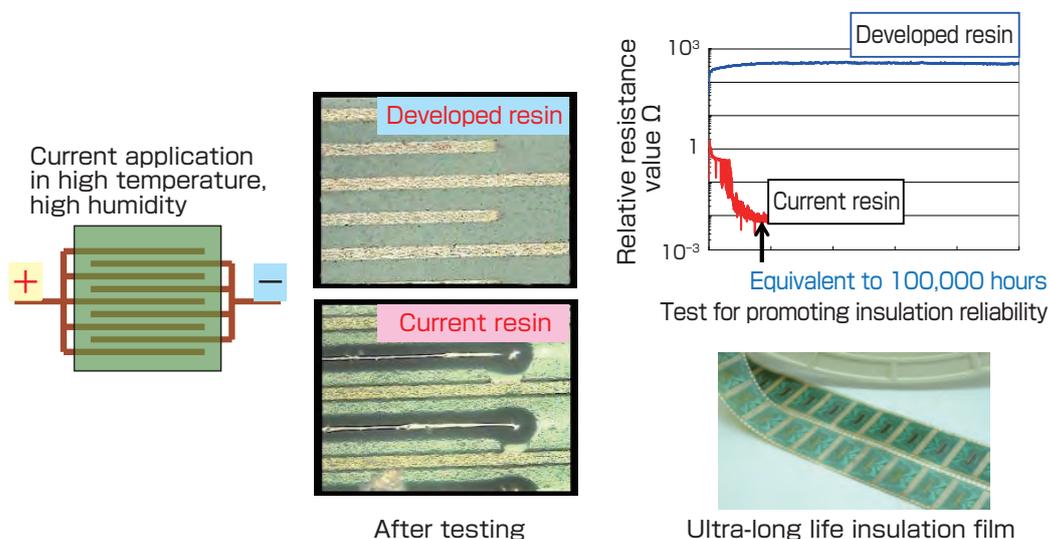


Fig. 12 Performance evaluation of the fabricated insulation material

insulation was not maintained. On the other hand, the film to which the newly developed resin was applied showed no deterioration after 100 thousand hours equivalent, showed more than two-digit higher insulating performance than the conventional products, and maintained the insulation property for a long time. This product enabled the size and weight reduction of electronic appliances, such as thinner LC displays. The newly adopted world share reaches 70 %.

7 Future development

The hydrogen peroxide oxidation technology developed this time is not limited to the manufacture of insulation film, but has the potential of contributing to all manners of functional chemical manufacturing using the oxidation technology. As a basic technology, we have the catalyst technology that allows environmentally benign oxidation using hydrogen peroxide. When realizing various products utilizing the hydrogen peroxide oxidation technology, we can achieve the goal at a short time because we have accumulated the knowledge and experiences of science and technology and therefore we are able to seek the essence of the reaction faster than the groups that are starting from zero. We are currently continuing to develop the basic technology.^{[22]-[24]} For example, we are developing the technology to create many epoxies within one molecule, technology to directly epoxidize the polymer, and technology to synthesize epoxy only among several reaction sites^[3]. The research continues spirally from basic research to product realization and then from application research looking at product realization to new basic research. The catalyst reaction developed several years ago is progressing to the step of realization now, and some has gone on to successful product realization. Currently, not only ultra-long life insulation films, but also the manufacture of diverse products including semiconductor sealants, next-generation adhesives, high-function surfactants, and radical polymers for battery materials are progressing to the stage of practical use or product realization.^{[25][26]}

8 Summary

The chemical industry is a major industry in Japan with shipment of about 40 trillion yen, additional value of about 15 trillion yen, and about 880,000 employees. Particularly, the world share of functional chemical products is high, playing an essential role mainly in the material supply for advanced assembly industry such as automobile and information/communication fields. On the other hand, the chemical industry dominates about 16 % of all domestic industries in carbon dioxide emissions, and 13 % in the production of industrial waste in the Japanese manufacturing industries. There is increasing recognition that the manufacturing technology with low environmental load is mandatory for the future chemical industry. For example, starting with the establishment of the Green Chemistry Workshop in the Chemical Society of Japan in 1999, the Green Sustainable Chemistry Network (GSCN) was

established in 2000 through industry-academia-government collaboration. Recently, the consciousness for clean chemical manufacturing methods has risen, and the “essential reduction of the amount of waste” was designated in the Johannesburg Plan of Implementation (WSSD 2020) at the 2002 World Summit on Sustainable Development (WSSD).

The strength of the Japanese chemical industry is that the individual companies engage in the manufacture of functional chemical products with their original know-how. Therefore, unless one has sufficient understanding of the sciences and possesses the highest level of basic technology, joint research is not possible and contribution cannot be made to realize the basic technology. Since we have the world’s highest level of elemental technology and scientific base for the highly selective activation of hydrogen peroxide, we were able to set clear chemical products and engaged in product realization through joint research with companies, and this led to product realization. Also, such ability to develop practical catalysts is not limited to hydrogen peroxide oxidation, but is an ability common to development and realization of any new catalysts. Currently, as new issues, we are taking on the direct manufacture from silicon raw materials using catalysts (using sand as a resource), manufacture of chemical products from carbon dioxide using catalysts, and direct manufacture of chemicals from oxygen and nitrogen in air (using air as a resource).

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The development to realize the ultra-long life insulation material using the hydrogen peroxide epoxidation technology was conducted as a joint research with Showa Denko K.K., and we thank Mr. Hiroshi Uchida. The author Sato found the potential of hydrogen peroxide oxidation technology described in this paper while he was studying at the Nagoya University, and developed it as basic technology and realization technology with co-authors Kon and Tanaka at AIST. We are grateful to Professor Ryoji Noyori and the students of the Nagoya University, as well as Hiromichi Shimada, Masato Tanaka, Yoko Usui, and Masanori Okoshi of AIST. Part of this research was supported by the New Energy and Industrial Technology Development Organization (NEDO), and we express our thanks to all those involved.

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explaining the scenarios and elemental technologies, for example: “The root of this research is the development of new catalysts that enables the industrial use of hydrogen peroxide as an oxidant, but for its realization, investigations and research for 1), 3), 4), 5) are necessary, as industrialization is not possible simply by creating a catalyst. In this paper, the integrating R&D for such elemental technologies will be explained.” Also, I think you should consider the structure for what kind of working hypothesis was set up for the development of innovative catalysts, what kind of facts were found as a result, and how the problems were solved by presenting the sequential stories from the perspective of halogen-free technology, organic-solvent-less technology, catalyst recovery/reuse technology, metal catalyst design technology, phase transfer catalyst design technology, and others. Moreover, I think you should make some revisions because the explanations about the application to adipic acid synthesis that you first started and the subsequent conversion to epoxy resin synthesis are rather unclear.

Answer (Yoshihiro Kon)

We reconsidered the five items of elemental technologies in the first draft and removed them. Instead, we positioned the organic-solvent-less technology, halogen-free technology, and metal catalyst design technology as the elemental technologies of the basic catalyst technology that enables oxidation by hydrogen peroxide, and newly added chapter 3. There, we described the process of setting a working hypothesis, verification by experiment, examination, and repeating the process, in line with the basic R&D style for catalyst development in chronological order, taking care that there will be no misunderstanding. Also, we added chapter 5 to set up the elemental technologies that must be considered for realization research and the integration system. In that chapter, we argued that the catalyst technology using hydrogen peroxide was the basic technology, and there were three milestones - target setting, cost, and scaleup – needed to realize the technology. Also, we reconsidered the structure of the overall argument, and described the basic catalyst technology in the newly set chapter 3, the example of adipic acid in chapter 4, and the setting of milestones based on failure with adipic acid in chapter 5, in chronological order to help the readers’ understanding.

Discussions with Reviewers

Overall

Comment (Toshimi Shimizu, AIST; Akira Kageyama, Research and Innovation Promotion Headquarters, AIST)

This paper describes the research scenario for the synthesis and integration of elemental technologies, from the development of new catalysts as a basic research program to the manufacture and product realization at bench plant scale toward the final product realization, for the hydrogen peroxide oxidation technology that was presented by the authors for the first time in the world as a specific example of green sustainable chemistry. It is a paper on integrated chemical technology, and it addresses the importance of catalyst technology in chemical industry as well as the importance of different viewpoints and technologies that are necessary in practical application of new catalyst technology in the industry. It is appropriate for publication in *Synthesiology*.

1 Structure of the scenario and elemental technology

Comment (Toshimi Shimizu, Akira Kageyama)

In the first draft, the authors list five elemental technologies for the scenario to achieve the goal: 1) setting of the target compound, 2) development of new catalysts, 3) establishment of oxidation process, 4) cost reduction, and 5) manufacture at bench plant scale and evaluation of the product. While these are important technological factors to raise the hydrogen peroxide oxidation technology to a practical and industrial level, the core of this paper is the R&D of new catalysts. If 1) ~ 5) are presented on the same line, they give the reader an impression that the five factors are equivalent in importance. I think there needs to be a structure in

2 Cost comparison

Question and Comment (Toshimi Shimizu)

The selection of desirable compounds that are the target of oxidation reaction, the design of the reaction plant for manufacturing, and the calculation of various costs are essential for industrialization. In the case in which the basic and functional chemicals are manufactured using the newly developed catalysts, the calculations of the costs of raw materials, catalysts, oxidants, facility investment, waste processing, and the value of final products are necessary. It is interesting to see what were the details (actual cost or the relative ratio) of the adipic acid manufacturing where the new method was withdrawn in comparison to the conventional method, as well as the details of the manufacture of ultra-long life insulation film (or epoxide) that was greatly successful. For example, if you present the particulars as a bar graph, I think the readers’ understanding will deepen about the solution of the cost problem in manufacture realization described by the authors.

Answer (Yoshihiro Kon)

As you indicated, we added Fig. 9 as a cost comparison of the most possible clarity. In Fig. 9, it is clearly shown that the failure of adipic acid was due to the fact that nitric acid was overwhelming cheaper than hydrogen peroxide, and the key was the cost difference of oxidants. On the other hand, the factors of the success of epoxy resin were that the functional chemical products themselves are high added value products including the raw materials, the oxidation by nitric acid was impossible since

the oxidation reaction technology became increasingly complex, and therefore, the oxidation became extremely higher in cost using the conventional oxidants (described as the conventional method in Fig. 11). In chapter 5, we discussed how the development of the innovative catalyst technology that enabled the manufacture of epoxy resin using hydrogen peroxide provided the cost advantage, since the cost of hydrogen peroxide was overwhelmingly less than that of the conventional method, and that led to practical realization.

Question and Comment (Akira Kageyama)

It is important from the perspective of green sustainable chemistry to show the amount of nitrous oxide emission that occurs due to the production of 2.2 million ton of adipic acid. Also, can you show the cost of hydrogen peroxide as an index against the cost of nitric acid used as an oxidant, as well as the treatment cost of emitted nitrous oxide? I think you should have a description of a rough cost comparison.

Answer (Shinji Tanaka)

The emission of nitrous oxide that occurred due to adipic acid production was 400 thousand ton in 1999 (described in chapter 1). The cost was calculated from the perspective of compound cost related mainly to the manufacturing process, and this was added to subchapter 5.3.

3 Relationship of the two types of catalysts

Question (Akira Kageyama)

Is the way of thinking that the first type of catalysts (metal catalysts) and the second type of catalysts (phase transfer catalysts) can be developed independently a general way of thinking in the field of catalyst technology? If so, this may show that only the authors were aware that an interaction of two catalysts with different functions might occur. Can you say that it is necessary to design the chemical and conformational (three-dimensional) structures of the catalyst taking into consideration such interaction when investigating the metal catalyst and phase transfer catalyst? Also, will this interaction have some effect on scale-up?

Answer (Yoshihiro Kon)

As you indicated, we became aware that there might be interaction between the two catalysts with different functions that we developed, and utilized the interaction of the catalysts actively to improve their activity. In the revised draft, we added the section on catalyst technology development in chapter 3, and described the facts in chronological order. The relationship between the interaction and catalyst structure was added to chapter 3. Although there are effects of interaction of the catalyst components in scale-up, since the explanation of the two types of catalysts was not correct in the first place, we added the explanation in subchapters 5.2 and 5.4 from the perspective of the necessity of reviewing the catalyst when conducting scale-up.

4 Selection of target chemical product

Comment (Akira Kageyama)

In the first draft, you write, "Appropriate functional chemical products were selected as targets....," but can you describe the standard for "appropriateness"? I think the E-factor shown in Fig. 8 is one of them, but can you tell us the approximate value of the E-factor that is the standard? I think this is an extremely important point when judging the application range of this technology, and it is an original point that only the authors can claim. Also, I think this standard includes the added value factor

of being able to prevent or control the negative functions of the products that accompany the use of chloride oxidants described later, not just the E-factor.

Answer (Yoshihiro Kon)

We think the "appropriate" standard is that the product has added value, has potential to sell, and possesses the potential for greatly reducing the E-factor theoretically. As an index, it must reduce the E-factor of the conventional method by one digit, and a ripple effect must be expected for the developed technology. We explained these in subchapter 5.1.

5 Epoxidation catalyst

Comment (Akira Kageyama)

I think the description of the epoxidation catalyst is the highlight of this paper, so please present the chemical structure of the catalyst and the reaction equation to obtain epoxide from olefin. Also, please show the detailed contents of the elemental technologies that were investigated and optimized to construct the integration system for this case. The first draft only describes the general theory, and what you did specifically is unknown. Since there are multiple elemental technologies, I think it is effective to present them using a fishbone diagram. Also, you write "the other type of catalyst," but can you use an expression that designates the function for this third type of catalyst, just as you did for the metal catalyst or the phase transfer catalyst?

Answer (Yoshihiro Kon)

The reaction equation of epoxidation was shown in Fig. 11 along with the description of adipic acid. To organize the milestones and elemental technologies in the progress toward realization, we created the fishbone diagram in Fig. 7 and offered an explanation in chapter 5.

I think the two types of catalysts for alcohol oxidation and adipic acid manufacture and the addition of the other type of catalyst for epoxidation are rather confusing. Therefore, we summarized the catalyst basic technology that enables oxidation by hydrogen peroxide in chapter 3. The third catalyst was called the "reaction site activating catalyst" to describe its function.

6 Future development

Comment (Akira Kageyama)

In future development, I think the authors have the knowledge and methodology to narrow down the candidate catalyst to some extent, compared to those who start from zero. Therefore, please describe the "methodology" for efficiently finding the optimal catalyst group. That is, how about stating that you have higher potential for achieving the objectives compared to those who start from zero, because the authors can use the accumulated knowledge and experience of science and technology?

Answer (Yoshihiro Kon)

As the methodology to efficiently find the optimal catalyst, as you indicated, I think we have the world's best understanding of the catalyst technology using hydrogen peroxide, all the way to the principle. We can quickly develop "specific" catalysts for target reaction by making minimum improvement to the basic technology based on this understanding, because we possess abundant knowledge and experience of the basic technology. I added this way of thinking to chapters 3~5 and 7. The knowledge of and experience with catalysts that we have accumulated do not stop at the hydrogen peroxide oxidation technology, but are common to the development of all practical catalysts.

Development of plastic certified reference materials (CRMs) to cope with restrictions on hazardous substances

— CRMs for analysis of heavy metals and brominated flame retardants regulated by RoHS directive —

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The RoHS directive had a significant impact on Japanese industry. Complying with this directive requires evaluating the raw materials, especially plastics, that are used in electrical and electronic equipment. However, few plastic reference materials (RMs) were appropriate for evaluation. In response to industry requests, we undertook rapid development of plastic RMs. First, we considered the development of RMs that were needed. To assign property values to candidate RMs, methods important for the homogeneity evaluation, digestion and determination were developed by various trials and errors. We aimed to register our calibration and measurement capabilities to the key comparison database in order to make our CRMs acceptable worldwide. In this paper we introduce our activities up until now including the distribution of CRMs inside and outside Japan.

Keywords : Restrictions of hazardous substances, RoHS Directive, plastics, certified reference materials (CRMs), analysis of heavy metals, analysis of brominated flame retardants

1 Introduction: Movement starting as response to the RoHS directive, a European regulation

The “RoHS directive” or the “Restrictions of the use of certain hazardous substances in electrical and electronic equipment”^[1] is one of the European Union (EU) directives which became effective in July 2006. In Japan, there was a great upheaval because the export of electrical/electronic equipment to EU would become impossible unless the requirements of the restrictions were met. Although this directive was for electrical/electronic equipment, the parts are made from raw materials and the final products are made by assembling the parts, and any parties of industries could not remain indifferent to the restrictions. The targeted hazardous substances were cadmium (Cd), mercury (Hg), lead (Pb), hexavalent chromium [Cr (VI)], polybrominated biphenyl (PBB), and polybrominated diphenyl ether (PBDE). The thresholds of restrictions (maximum values tolerated) were 100 mg/kg for Cd and 1000 mg/kg for the other substances. The PBB and PBDE belong to the group called brominated flame retardants, and their structural equations are shown in Fig. 1. There are many isomers depending on the number and position of bromine (Br). Since this was not a restriction on the total amount, a problem could develop even if a single part contained high concentration. It can be said that it is a rather unreasonable restriction on concentration.

The objectives of the RoHS directive are to remove the differences in legal regulations among the EU nations pertaining to the restriction of hazardous substances used in electrical/electronic equipment, as well as the protection of

health of users, the protection of health of workers involved in the processing of waste electrical/electronic equipment, the reduction of environmental and resource loads, and the promotion of resource recovery. Although the RoHS directive is just one of several restrictions, it should be considered as part of the movement for environmental protection. Moreover, not limited to electrical/electronic equipment, there are laws established for the restriction of use of hazardous substances, the quality labeling of products, and the recovery of waste products in many countries along the line of these objectives, and the basic principle is to stop using hazardous or specific substances considering the future. Therefore, the demand for measurement of hazardous or specific substances in products is expected to increase in the future.

The RoHS directive was revised in 2001 (commonly called RoHS2 or new RoHS; the new directive has replaced the old as of January 3, 2013).^[2] In the new directive, the restriction on the range of target increased, but the compounds under restriction and the concentration thresholds did not change. Other than the RoHS directive, there are the WEEE directive (directive on waste electrical and electronic equipment),^[3] the ELV directive (directive on end-of-life vehicles),^[4] and the REACH regulation (the EU regulation on the registration, evaluation, authorization and restriction of chemicals)^[5] which is a comprehensive regulation of chemical substances. Also, JIS C 0950:2008, which is commonly called the Japanese RoHS or J-Moss, was adopted to regulate the labeling of the content of specific substances. In the present paper, we discuss the development of RMs at the National Metrology Institute of Japan (NMIJ)

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standards, and therefore, we were engaging in research with priority on traceability to the international system of units (SI) which are necessary for international activities. “Traceability” is the property of a measurement result whereby the result can be related to a superior standard through a chain of assignments of property values, and when it is used as an adjective, the terminology “traceable” is used. To distinguish from traceability related to food origin recording, it is formally called metrological traceability. The Polymer Standards Section, Advanced Material Division (at the time) had abundant experiences in quantification of organic substances coexisting in plastic.

In the supply chain, the communication of data from the raw material stage was important, and the system construction for such communication was urgently required. However, considering that the final responsibility would lie on the direct supplier which supplied the products to EU, it was necessary for the supplier to ensure that the restricted substances in the final products were below threshold to respond properly to the RoHS directive, and therefore, precise analysis of them was needed for verification. To respond to these problems, an analytical method which was internationally accepted was particularly necessary. It is not easy to objectively show that one’s own analytical method or result is appropriate and accurate. However, for a laboratory itself to analyze the CRM traceable to the appropriate reference and to show that the results are in agreement with the certified value (content or property value given in the certificate issued with the CRM) is one way of conducting general and effective internal-control of precision (to check whether the analytical value can be obtained appropriately by oneself).

For this issue, there were very few appropriate CRMs in 2003. It is said that the authorities who set forth the EU restrictions make decisions based on high ideals especially for the environment, and in fact, the RoHS directive was a restriction set forth with primary focus on ideals. That is, in the course of setting the directive, specific methods for investigating the compliance to the restriction were left behind, and the availability of appropriate CRMs was not considered at all. Meanwhile, it should be mentioned that there were two CRMs available [BCR-680 and BCR-681 from the Institute for Reference Materials and Measurements (IRMM)] which were given certified values for heavy metals and others in PE (polyethylene) resin. However, these CRMs were not created in consideration of the RoHS directive; therefore, the concentration levels for the restricted substances did not comply with the RoHS directive, and it did not comply at all with the restriction for brominated flame retardants which were ones of the six restricted substances.

There was no international standard method for analysis as a premise to use RMs, and the work of setting such a standard was pushed. Japan actively participated in this movement. The IEC 62321:2008^[7] was the first IEC standard for the quantification of six restricted substances, and NMIJ contributed by providing the candidate RMs (clearly written as NMIJ CRM 8112-a and

NMIJ CRM 8113-a in IEC 62321:2008) which were being developed, as samples for inter-laboratory comparisons in the early stages of the standard setting. This standard was revised as family type standards in the regular revision of 2013, where the contents were updated and the future diversification of RoHS regulations was considered. The updates were: IEC 62321-1:2013 (Introduction and overview); IEC 62321-2:2013 (Disassembly, disjunction and mechanical sample preparation); IEC 62321-3-1:2013 (Screening - Lead, mercury, cadmium, total chromium and total bromine using X-ray fluorescence spectrometry); IEC 62321-3-2:2013 (Screening - Total bromine in polymers and electronics by Combustion - Ion chromatography); IEC 62321-4:2013 (Mercury in polymers, metals and electronics by CV-AAS, CV-AFS, ICP-OES and ICP-MS); and IEC 62321-5:2013 (Cadmium, lead and chromium in polymers and electronics and cadmium and lead in metals by AAS, AFS, ICP-OES and ICP-MS).

The awareness of the problem was high in the Ministry of Economy, Trade and Industry (METI) which held jurisdiction over issues related to the manufacture and export of electrical/electronic products. Therefore, with METI support, we were able to conduct the project “Research for Infrastructure Development on Environment-Conscious Design Promotion” of the New Energy and Industrial Technology Development Organization (NEDO) for two years (2005 to 2006), and NMIJ was able to develop several CRMs in a short period. For the movements for the new RoHS2, METI is engaging in activities such as holding seminars with the industrial associations.

2.2 Why plastics?

As mentioned earlier, the target substances of the RoHS directive were Cd, Hg, Pb, Cr (VI), PBB, and PBDE, and the thresholds of restrictions were 100 mg/kg for Cd and 1000 mg/kg for other substances. Most of the interests were focused on these substances in plastics, and the CRMs with a plastic matrix were in demand. The background for the demand of plastic CRMs was as follows: many plastic parts are used in electrical/electronic equipment; historically, restricted substances had been intentionally introduced to plastic for coloring and flame retardation; although intentional introduction of such substances is not done today, old plastics may become mixed in the recycling process; and there were hardly any CRMs with a plastic matrix at the time.

Due to the globalization and borderlessness of the market, the demand for traceability is increasing for chemical standards. When traceability is demanded, an analysis certificate in which the analytical values by testing laboratories can be internationally and mutually recognized is essential. Therefore, the provision of CRMs with traceability which complies with the international Mutual Recognition Arrangement (MRA) for the metrological standards of the International Committee for Weights and Measures (CIPM) under the Metre Convention is important. The developed RMs were of the following:

acrylonitrile butadiene styrene (ABS) resin, polypropylene (PP) resin, polyvinyl chloride (PVC) resin, and polystyrene (PS) resin which are plastics used widely today. Most of the plastics used in electrical/electronic equipment were one of these types of resin.

As the matrix for CRMs for heavy metal analysis, we considered PE or ABS resins which were frequently used in electrical/electronic equipment, and the ABS resin was selected for the first CRM because the CRMs of BCR which existed at that time were made of PE resin. CRMs of PP and PVC resins were produced later.^[8] Brominated flame retardants were mainly used in the body of TV sets, and they were mostly made of PS type plastic [ABS resin, high-impact polystyrene (HIPS) resin, and PS resin]; therefore, a candidate was selected among these for the brominated substances. For selecting which of the PS types would be used, we considered the ease of handling during analysis. For heavy metals, the sample could be digested completely since the analysis was for elements. On the other hand, for brominated flame retardants, complete digestion could not be applied since the analysis was for molecules; therefore, an appropriate extraction method was necessary. Since it was known that insoluble components were present when ABS and HIPS resins were dissolved in solvents, first, PS resin was selected because a homogenous solution could be made, and CRMs made of PVC resin were later produced.

2.3 Scenario from the international comparison to CMC registration

Since the impact of the RoHS to plastics was great, NMIJ focused on plastics and started the activities to develop and provide CRMs as soon as possible.^{[9][10]} At the same time, it was necessary that the CRMs be RMs which complied with CIPM MRA, and that the analysis results would be accepted worldwide. For the compliance of CRMs with CIPM MRA, the followings are needed : specifically, a management system of CRM production (management system based on standards or guides such as the ISO/IEC 17025 or ISO Guide 34) is constructed, and its technological capability is approved by several overseas experts in a so-called peer-review process. Furthermore, the ability to create the CRMs, a part of the calibration and measurement capability (CMC), must be claimed to the KCWG [one of the working groups (WGs) of the CCQM for Key Comparisons and CMC Quality] with available evidences from international comparisons (will be explained in subchapter 4.3), and then must be listed in the Key Comparison Database (KCDB)^[11] of the International Bureau of Weights and Measures (BIPM). When the CRM development was started, activities towards CMC registration were done alongside the development. The details will be discussed later.

2.4 Steps for deciding the RM matrices, target analytes, concentrations, and forms

Since the analytical methods for heavy metals and brominated

flame retardants are generally different, we decided to create different CRMs. However, for heavy metal analysis, the brominated flame retardants were included from the second series of NMIJ CRM 8112-a for heavy metal analysis, to leave possibilities for the future. The brominated flame retardants were restricted as compounds, and there should be no problem if total Br was measured and the value was sufficiently low. Since the minimum Br content in the case of 1000 mg/kg for compounds occurs in the case of monobrominated diphenyl ether (details will be explained later), the added compounds was set as decabromodiphenyl ether (DBDE or BDE-209) and its quantity added was determined. There were several candidates for the heavy metal compounds to be added to the CRM, and available compounds were sought thinking that fine powder would be desirable for mixing homogeneously with plastic. Considering the ease of handling of CRMs, lead chromate (PbCrO₄) and cadmium oxide (CdO) were selected since they were not restricted by the Poisonous and Deleterious Substances Control Law [chromium (III) acetylacetonate was also used from the second series for heavy metal analysis]. Mercury (II) sulfide (HgS) was selected as Hg compound to be added to the second series for heavy metal analysis from the same perspective.

There were two types of concentration: one around the restriction value (called high concentration); and the other about one-tenth of that value (called low concentration). In the first series for heavy metal analysis, the concentrations for Cd was set at slightly over 100 mg/kg and for Pb slightly over 1000 mg/kg, and the concentration for Cr(VI) was about 250 mg/kg (each concentration in the low concentration was one-tenth of such a value). For judging the adequacy to the restriction, we designed the concentration in CRM to be lower than the restriction value from the second series for heavy metal analysis, because determining whether analytical values were lower than the restriction value would be easier.

For the concentration of brominated flame retardants in RMs, we investigated how it should be chosen considering the threshold, and decided as follows. Of the target substances PBB and PBDE, the one with the lowest Br content (mass fraction) is monobrominated diphenyl ether (molecular weight 249.1) at 32 %. Therefore, when conducting simplified screening using Br measurement by non-destructive X-ray fluorescence (XRF) analysis, the 1000 mg/kg regulation for PBB and PBDE could be kept, if it was evaluated assuming that monobrominated diphenyl ether would be contained only as Br compounds. When DBDE was used as brominated flame retardants, the Br content (mass fraction) of 32 % would correspond to DBDE of 385 mg/kg. In the NMIJ CRM which contained DEDE only as Br compounds, it was designed at slightly lower concentration than this value. That is, we developed NMIJ CRM 8108- a (polystyrene) with DBDE certified value of 317 mg/kg, and as the following lots, developed NMIJ CRM 8108- b (polystyrene) with DBDE certified value of 312 mg/kg and

NMIJ CRM 8109-a (polyvinyl chloride) with DBDE certified value of 333 mg/kg. The reason for selecting the DBDE as the added brominated flame retardant was because DBDE was advantageous in accurately determining the certified value of CRM since pure DBDE was readily available. We further developed NMIJ CRM 8110-a (polystyrene, high concentration) with DBDE certified value of 886 mg/kg. This could be used for verifying linearity when drawing a calibration curve.

There were two RM forms for heavy metal analysis: pellet (small rods or round particles of about 0.01 g to 0.03 g) for wet analysis; and disk (diameter of 3 cm and thickness of 2 mm) due to strong demand for non-destructive XRF analysis. On the other hand, there was only the disk form for brominated flame retardant. The diameter of the disks was the size of a sample holder of an ordinary XRF analysis instrument. In case of plastics, since the result of the XRF analysis was dependent on thickness, we set the thin thickness of 2 mm considering the variation in thickness of samples to be analyzed, and more than one disk could be stacked together for thicker samples if necessary.^[12] For the manufacturing method, kneading and injection molding were done (hot press was used for the first series of NMIJ CRM 8105-a and 8106-a) (Fig. 3).

2.5 Cooperating institution and manufacturing method

It was necessary to find a cooperating institution which would help us manufacture the candidate RMs. We requested preliminary consideration to Y.K. Kobunshi Giken on December 2003. After visiting the actual plant and holding thorough meetings, we witnessed the kneading process, and the manufacturing was conducted while maintaining close communication. Later, after the second series for heavy metal analysis (NMIJ CRM 8102-a, 8103-a, 8105-a, and 8106-a), we searched for a different cooperating institution because

it was necessary to increase the size of the production lot. In September 2005, preliminary kneading was conducted with the Chemicals Evaluation and Research Institute, Japan. We went to the plant for each manufacturing to communicate with the workers to achieve better homogeneity.

While manufacturing was done by a universal method, kneading/extruding was done three times to ensure homogeneity. Preliminary kneading/extruding was conducted to check whether the homogeneity was sufficient after kneading/extruding three times. To avoid loss of homogeneity due to contamination from the kneading extruder or surrounding environment, optimum care was taken to meticulously cleanse the kneading extruder at a level not normally done.

Specifically, the details of manufacturing candidate RMs for heavy metal analysis are as follows. The commercially available raw resin pellets and powdered compounds (cadmium oxide, lead chromate, chromium (III) acetylacetonate, mercury (II) sulfide, DBDE, and others) were mixed, and the mixture was formed into pellets again using the kneading extruder. Furthermore, the reformation into pellets was repeated twice to manufacture the candidate RM of high concentration. The commercially available raw resin pellets were added again to this pellet, and the stirring, mixing, and pellet forming processes were repeated three times using the kneading extruder to manufacture the candidate RM of low concentration. The disk form candidate RMs were manufactured by hot press or injection molding methods using the aforementioned candidate RMs as the raw materials. For PVC resin, the base resin was made by adding the plasticizing agent diisononyl phthalate (DINP), stabilizer, etc. to the commercial PVC resin; then, powdered cadmium oxide, lead chromate, chromium (III) acetylacetonate, and mercury (II) sulfide were mixed with the base resin, and the mixture was

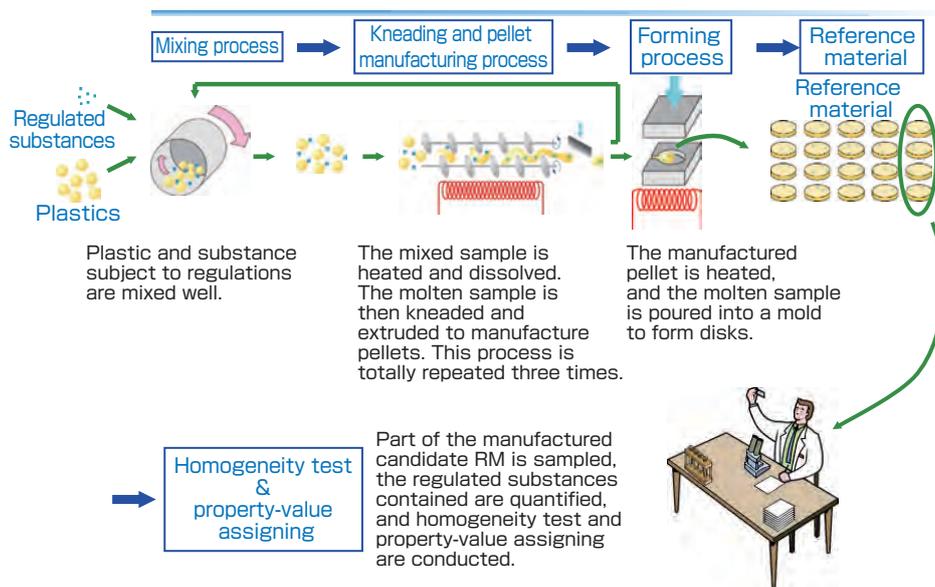


Fig. 3 Manufacturing process of plastic RMs (example)

Table 1. Performance in the acid and microwave digestion processes which were attempted^[13]

| Acid used in digestion (number in parenthesis indicates the quantity used) | Degree of digestion achieved | Comment |
|---|------------------------------|--|
| 95 % H ₂ SO ₄ (4 mL) | × | Turned into highly viscous blank solution |
| 95 % H ₂ SO ₄ (4 mL) + 70 % HNO ₃ (4 mL) | ◎ | |
| 95 % H ₂ SO ₄ (4 mL) + 60 % HNO ₃ (4 mL) | ◎ | |
| 60 % HNO ₃ (8 mL) | × | |
| 60 % HNO ₃ (5 mL) + 30 % H ₂ O ₂ (3 mL) | × | |
| 60 % HNO ₃ (5 mL) + 60 % HClO ₄ (3 mL) | △ | To achieve complete digestion, three microwave heating processes and two microwave heating processes were necessary. |
| 60 % HNO ₃ (5 mL) + 60 % HClO ₄ (2 mL) + 48 % HF (1 mL) | △ | |
| 60 % HNO ₃ (5 mL) + 30 % H ₂ O ₂ (2 mL) + 48 % HF (1 mL) | × | |
| 70 % HNO ₃ (8 mL) | ○ | To achieve complete digestion, the digestion containers used in a single operation had to be reduced to 5 instead of 10 used normally. |

Sample: 0.1 g ABS resin pellet CRMs; Digestion device: ETHOS PLUS and ETHOS 1, Milestone

◎: Complete digestion was achieved with one microwave heating process.

○: Complete digestion was achieved with one microwave heating process (however, number of digestion containers which could be used in a single operation was limited).

△: Complete digestion was achieved by using both microwave-heating and microwave-drying processes.

×: Complete digestion could not be achieved by one microwave heating process.

formed into pellets using the kneading extruder. Using the pellets formed, the stirring, mixing, and pellet reforming processes were repeated two more times. For the RMs for brominated flame retardant analysis, disk-shaped candidate RMs were manufactured by the injection molding method using the pellets produced in the same way as those for the heavy metal analysis (for high concentration).

3 Development of the analytical method

Quick development of CRMs was demanded, and analysis was important after the manufacture of candidate CRMs. Although we had technological background which we accumulated over the years and minimum budget, those were not enough for analytical evaluation of the candidate CRMs. In particular, investigation of a digestion method was important, and we engaged in various trials-and-errors, as the situations differed according to individual samples (Table 1).^[13] For creating the CRM, multiple digestion methods and quantification ones had to be used, and it was necessary to develop alternative methods and to increase reliability, even if the best method was obtained. For Cr, the restriction was for hexavalent chromium, but there was no method for accurately analyzing the hexavalent chromium in plastics, and establishing such a method was considered difficult. Therefore, we conducted quantification of the total chromium. If the concentration of the total chromium was 1000 mg/kg or less, that of hexavalent chromium would, of course, be 1000 mg/kg or less.

3.1 Evaluation method for homogeneity

Homogeneity is extremely important for RM, and the evaluation method was considered from the stage of manufacture of the

candidate RMs. When filling the bottle with RM material after kneading/extruding, the order of filling the bottles was recorded, and the bottles from which the samples would be taken for homogeneity evaluation were selected from all bottles by stratified random sampling. We attempted homogeneity evaluation within a bottle and among the bottles assuming that sampling would be done once from one bottle purchased by the user (for disks, within disk surface and among disks). The homogeneity evaluation did not have to use quantitative values, and priority was given to making quick comparison among the samples, and it was sufficient as long as the values were proportional to the concentrations.

The homogeneity evaluation method is shown below using Cr of NMIJ CRM 8103-a (high concentration) as an example. For evaluation, 12 bottles were selected of about every 25th bottle among samples numbered by order of bottling. The measurement for homogeneity evaluation was done as follows. From the 12 bottles, 0.10 g each was sampled once, samples were digested according to an established method, and quantification was done by ICP-MS. The measurements were taken for the two isotopes of chromium (Cr-52 and Cr-53). The whole process starting with sampling was repeated again. To ensure accurate homogeneity, absolute values were not sought in the measurement.

The measurement results are shown in Table 2. The variance of measured value for the 12 samples of Cr-52 in the first round (0.74²) could be thought as a combination of variance among bottles, variance of measurement error, and variance within a bottle (non-repeated measurement). The standard deviation obtained from the combination of the variances would represent homogeneity, because the analytical value for one sampling

Table 2. Measurement example of Cr homogeneity test for NMIJ CRM 8103-a (high concentration) (the unit for each value is mg/kg)*1

| Bottle | First round | | Bottle | Second round | |
|---------------------------------|--|--|---------------------------------|--|--|
| | Concentration estimated from Cr-52 intensities | Concentration estimated from Cr-53 intensities | | Concentration estimated from Cr-52 intensities | Concentration estimated from Cr-53 intensities |
| H001-1 | 273.18 | 272.06 | H001-2 | 274.95 | 274.67 |
| H027-1 | 272.65 | 272.22 | H054-2 | 273.59 | 273.34 |
| H054-1 | 272.89 | 271.62 | H108-2 | 274.89 | 273.91 |
| H081-1 | 273.33 | 272.87 | H162-2 | 274.69 | 274.34 |
| H108-1 | 273.07 | 271.53 | H027-2 | 273.42 | 272.92 |
| H135-1 | 271.91 | 271.50 | H081-2 | 273.13 | 272.93 |
| H162-1 | 272.29 | 271.96 | H135-2 | 274.41 | 272.67 |
| H189-1 | 274.62 | 273.12 | H189-2 | 275.09 | 273.05 |
| H216-1 | 273.29 | 273.82 | H216-2 | 273.76 | 273.26 |
| H270-1 | 272.54 | 273.26 | H243-2 | 274.08 | 272.11 |
| H243-1 | 272.42 | 273.37 | H270-2 | 273.92 | 272.82 |
| H275-1 | 273.91 | 273.04 | H275-2 | 274.54 | 273.28 |
| Average value | 273.01 | 272.53 | Average value | 274.21 | 273.28 |
| Experimental standard deviation | 0.74 | 0.81 | Experimental standard deviation | 0.65 | 0.72 |

*1 Calibration curve was drawn using standard solutions, and the values in the table are different from the certified value due to the matrix effect of samples.

from a certain bottle will be given as the certified value. The homogeneity was calculated based on the average of four dispersions of two rounds and two isotopes, so the value would be as appropriate as possible. The relative standard uncertainty of homogeneity was 0.27 %, and it was confirmed that there was no problem in homogeneity.

For the homogeneity evaluation of the disks,^[14] for example, in the case of NMIJ CRM 8115-a (low concentration), 16 disks were selected at about equal intervals in the order of manufacture among all manufactured disks, Cd, Cr, Hg, and Pb were measured using the XRF analysis method, and the uncertainty arising from homogeneity was calculated from the variation in strength corresponding to each element. The homogeneity evaluation of Pb within disk surface was done using the XRF analysis method, and this was added to the uncertainty arising from homogeneity among disks for each element. These would be ultimately included in the uncertainty of each certified value of CRMs.

3.2 Investigation of the digestion method and the development and evaluation of the quantification method

For assigning the property values of CRMs, we decided to combine a method recognized as meeting the requirements of a primary method of measurement [only the isotope dilution mass spectrometry (IDMS) can be applied to this case] and one or more carefully evaluated methods. This policy would be generally employed to maintain reliability of NMIJ CRMs. Although the IDMS method cannot be applied in all cases, it is essential wherever it can be applied.

Specifically, the methods employed for heavy metals is as follows. For pellets and disks of all types, the quantification by isotope dilution ICP-MS was done after microwave digestion with sulfuric acid and nitric acid. In the case of pellets, two more methods were used: microwave digestion (one of the following three methods: method using sulfuric acid and nitric acid, one using nitric acid and perchloric acid, or one using 70 % nitric acid), and open-vessel dry-ashing (one of the following two methods: method using nitric acid and hydrogen peroxide or one using nitric acid). For instrumental analysis, ICP-MS and ICP-OES which have different principles were combined with either digestion method. As a result, the quantification values were calculated using multiple methods, which were mutually independent, to increase reliability. As a premise for deciding the methods, the digestion method mentioned before^[13] was investigated, as well as the effects of acid as matrix when measuring the digested solution by ICP-MS were investigated.^[15]

On the other hand, the quantification of brominated flame retardants as molecules was different from the quantification of heavy metals as elements: we had to ensure that the original molecule would not be broken. For such a purpose, the appropriate digestion, separation, and quantification methods were decided taking into consideration the chemical characteristics of both the analyte (component which is targeted for analysis) and the matrix.^[16]

For brominated flame retardants, tetrahydrofuran (THF), toluene, and chloroform etc. were considered as candidate solvents to dissolve PS. As a result of investigating the solubility of DBDE in these solvents, it was found that all dissolved at 1

mg/mL or more. Of these, when THF without any stabilizer was used, there was a possibility that DBDE would be decomposed due to minute amount of decomposed products of THF (using old solvents, decomposition actually occurred during gas chromatographic analysis). Therefore, PS was dissolved using toluene and chloroform.

The quantification of brominated flame retardants was done by the isotope dilution method and standard addition method. The isotope dilution method is a method which should be done as far as possible in principle, as mentioned before. With the standard addition method, PS was separated by adding a poor solvent (solvent with low solubility of target solute; methanol was selected) for PS into the solution prepared by dissolving RM, and the supernatant solution was collected and concentrated; finally the content of DBDE was measured. Here, the recovery should be considered, but pretreatment was carried out after adding several different amounts of DBDE to the RMs, and using these solutions, the contents were calculated using the standard addition method. Although this method is time consuming, it is a determination method where low recovery was not a concern.

Since there were many isomers of PBDE and PBB used as brominated flame retardants, it was difficult to determine the individual property values by adding all types of individual compounds. When the amount of Br per mass is high, the effect as flame retardant is high. Since such substances have been used, we selected the DBDE with the largest amount of Br per single molecule as the CRM additive. The effect of impurities during DBDE quantification was examined.^[17]

4 Metrological traceability, reliability of certified value, and others

4.1 Need for metrological traceability

Since voices were raised for the lack of RMs necessary for tests to respond to the RoHS derivative, some types of RMs were created by some private companies and the Japan Society for Analytical Chemistry. These were provided along with the CRMs developed by NMIJ, and it should be mentioned that they played a role different from the CRMs of NMIJ.

However, for the analytical value in response to the RoHS directive to be internationally accepted, it is important that the analysis is conducted by laboratories which obtained laboratory accreditation based on ISO/IEC 17025 etc. from accreditation bodies. The lab accredited for ISO/IEC 17025 did exist at the start of plastic CRM development at NMIJ, though smaller in number compared to now. Traceability is one of the requirements for lab accreditation, and the importance of CRMs was high for realization or verification of traceability at the lab. The CRM used there had to be accepted worldwide, and NMIJ CRMs were expected to play such a role, and this position has not changed even now.

Table 3-a. NMIJ CRM 8102-a: Case of ABS resin pellet for heavy metal analysis (Cd, Cr, Pb; low concentration)

| | Certified value* ¹ Mass fraction (mg/kg) | Expanded uncertainty* ¹ Mass fraction (mg/kg) |
|----|--|---|
| Cd | 10.77 | 0.20 |
| Cr | 27.87 | 0.35 |
| Pb | 108.9 | 0.90 |

*¹ Assigning done independently by NMIJ

| | Median of collaborating analysis Mass fraction (mg/kg) | Estimated value of standard deviation for whole distribution Mass fraction (mg/kg) |
|----|--|--|
| Cd | 10.31 | 0.53 |
| Cr | 26.64 | 1.64 |
| Pb | 106.6 | 5.5 |

Table 3-b. NMIJ CRM 8103-a: Case of ABS resin pellet for heavy metal analysis (Cd, Cr, Pb; high concentration)

| | Certified value* ¹ Mass fraction (mg/kg) | Extended uncertainty* ¹ Mass fraction (mg/kg) |
|----|--|---|
| Cd | 106.9 | 1.40 |
| Cr | 269.5 | 4.5 |
| Pb | 1084 | 9.6 |

*¹ Assigning done independently by NMIJ

| | Median of collaborating analysis Mass fraction (mg/kg) | Estimated value of standard deviation for whole distribution Mass fraction (mg/kg) |
|----|--|--|
| Cd | 105.4 | 4.4 |
| Cr | 267.4 | 13.0 |
| Pb | 1080 | 31 |

For metal standard solutions, the standard solutions supplied as the calibration standard solutions for Japan Calibration Service System (JCSS) based on the Measurement Law in Japan or its primary standards which NMIJ certified was directly used to maintain traceability. Since there were no JCSS standard solutions for brominated flame retardants, the purity of DBDE was originally determined using the HPLC method.

NMIJ constructed the management system based on ISO/IEC 17025 and ISO Guide 34, and has received the ASNITE accreditation from the International Accreditation Japan (IA Japan) of the National Institute of Technology and Evaluation (NITE). The NMIJ CRMs have been added to the accreditation scope as they are developed.

4.2 Analysis of interlaboratory comparison in Japan

With the participation of 19 testing labs and analytical institutes (18 institutes for Cr), analysis of interlaboratory comparison was conducted for Cd, Cr, and Pb in heavy-metal-containing ABS resin RMs [two materials for high level (NMIJ CRM 8103-a) and low level (NMIJ CRM 8102-a)] (from December 2004 to February 2005). Each median and the standard deviation of overall distribution estimated on the basis of the dispersion from the median were mentioned in the NMIJ CRM certificates as information. These values are shown in Table 3 along with the certified values. There were many acids used for sample digestion: nitric acid; nitric acid and hydrogen peroxide; nitric

acid and sulfuric acid; nitric acid and perchloric acid; nitric acid, sulfuric acid, and hydrogen peroxide; nitric acid, hydrofluoric acid, and boric acid; nitric acid, sulfuric acid, perchloric acid, and hydrochloric acid; fuming nitric acid, nitric acid, and perchloric acid; sulfuric acid; sulfuric acid/hydrogen peroxide; and sulfuric acid and nitric acid/hydrogen peroxide. There was also an institute which used the combination of dry ashing, alkali fusion, and hydrochloric acid extraction. The instrumental measurement methods were ICP-OES, ICP-MS, flame atomic absorption spectrometry, and electric thermal vaporization atomic absorption spectrometry. What distribution would the values obtained by different institutions using different acids and instrumental measurement methods have was useful information for knowing the reality of analysis for the users of the particular CRMs. For the testing labs and analytical institutes which participated, this exercise took a role much like a proficiency test. Of course, we were conducting determination of certified values with confidence, and agreement among the results by multiple methods were confirmed, but we had to be particularly careful since any apparent disagreement with the analytical value of labs might cause unnecessary confusion.

4.3 Proposal of international comparison to the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) under the Metre Convention

4.3.1 International comparisons under the Asian Collaboration on Reference Materials (ACRM) among Japan, China and Korea

The Asian Collaboration on Reference Materials (ACRM) is organized among three national metrology institutes (NMI) of Japan, China, and Korea, and the working groups (WGs) are set up for each technological field. WG3 specializes in the discussions about the RoHS directive, and Akiharu Hioki, one of the authors, was the convener, who is succeeded by Shigetomo Matsuyama. As activities under WG3, several comparisons were conducted when the samples of candidate RMs being developed in each country at the candidate RM stage were exchanged. In the field of RM for heavy metal analysis, WG3 has conducted interlaboratory comparisons for two types of ABS resin candidate RMs (later NMIJ CRM 8112-a and NMIJ CRM 8113-a) of NMIJ (2006), two types of PP resin candidate RMs of the National Institute of Metrology, China (NIM) (2007), and two types of PP resin candidate RMs of the Korea Research Institute of Standards and Science (KRISS) (2007). In the field of RM for brominated flame retardant analysis, three interlaboratory comparisons were planned of DBDE concentration in a toluene solution (2008), of DBDE concentration in PE (2009), and of DBDE concentration in HIPS (2010). Through such comparisons, the capability of each institute was confirmed, and sometimes they contributed to improving the skills.

4.3.2 International comparison of Consultative Committee for Amount of Substance: Metrology in Chemistry and

Biology (CCQM) under the Metre Convention

Under the Metre Convention, a technical consultative committee is organized for each metrology field, and CCQM is for the chemical metrology field. The Inorganic Analysis WG (IAWG) and the Organic Analysis WG (OAWG) are established as WGs in the CCQM. Through the comparisons and discussions at the ACRM meetings, enthusiasm for conducting a global level comparison increased, and pilot studies of CCQM/IAWG were proposed jointly by three countries, Japan (NMIJ), China (NIM), and Korea (KRISS): the proposal was adopted. This study CCQM-P106 (determination of the mass fractions of Cd, Cr, Hg, and Pb in PP) was given the position of benchmark in the IAWG as a result of active discussion proposed by NMIJ, and the results could be used as evidences to underpin CMC registration. It was, in fact, considered equivalent to a key comparison under the agreement of the participants of the study. The results are published in an international journal.^[18] An example of the results is shown in Fig. 4.

For the RM for brominated flame retardant analysis, although CMC claims were not aimed, equivalency was demonstrated in the CCQM-P114 (quantification of some of PBDE and PBB in PP) of CCQM/OAWG.^[19] The results are shown in Fig. 5 [Lab No. 4 indicates NMIJ, which participated only in the part of DBDE (BDE-209)].

4.4 Peer reviews based on CIPM MRA and CMC registration to the BIPM Key Comparison Database (KCDB)

NMIJ demonstrated the capability through (1) developing CRMs under the management system based on ISO, (2) receiving peer reviews, and (3) submitting good results for CCQM-P106, the international comparison of CCQM (in general, a key comparison is necessary, but as a

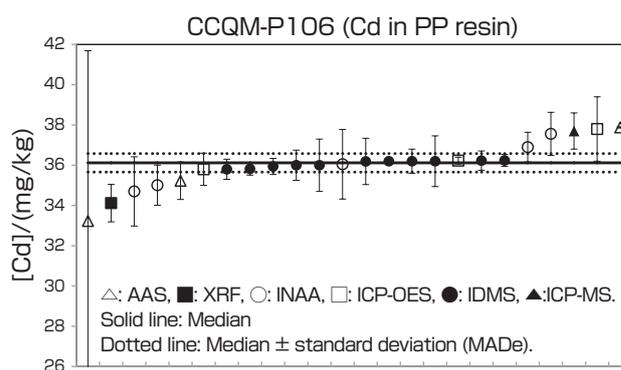


Fig. 4 Result of Cd in CCQM-P106, the international comparison for the quantification of four metals in PP resin

Horizontal axis shows the participating institutes, and NMIJ is ninth from the right. AAS: Atomic absorption spectrometry, XRF: X-ray fluorescence spectrometry, INAA: Instrumental neutron activation analysis, ICP-OES: Inductively coupled plasma optical emission spectrometry, IDMS: Isotope dilution mass spectrometry, ICP-MS: Inductively coupled plasma mass spectrometry. Half length of each bar indicates the expanded uncertainty (the coverage factor is 2 for almost all cases).^[18]

matter of fact this pilot study was considered equivalent to a key comparison). Three requirements from (1) to (3) were fulfilled, CMC registration to the BIPM KCDB was made, and CMCs for heavy metal analysis in plastics were registered. The registration of CMCs (Fig. 6) in the KCDB is one of the goals for CIPM MRA, and the corresponding metrological traceability of NMIJ is valid throughout the world through the standards entered therein.

5 Dissemination of the CRMs and following activities

5.1 State of dissemination

Some examples of packages of the developed NMIJ CRMs are shown in Fig. 7. The numbers per fiscal year of disseminated plastic CRMs for heavy metal analysis and brominated flame retardant analysis are shown in Fig. 8. The cumulative totals up to FY 2013 of the disseminated plastic CRMs were 1102 units for heavy metal analysis and 600 units for brominated flame retardant analysis. In general, since CRMs like the plastic CRM in response to the RoHS directive are not used daily, the dissemination number of each CRM is fairly close to the number of institutions which purchased it. The demand

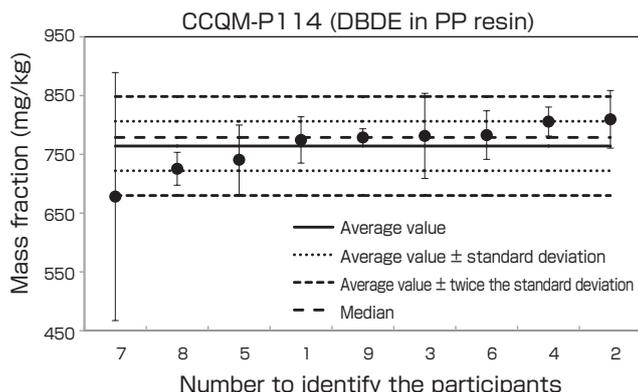


Fig. 5 Result of CCQM-P114, the international comparison for the quantification of DBDE in brominated flame retardant (institution number for NMIJ is 4) Half length of each bar indicates the expanded uncertainty (the coverage factor is 2 for almost all cases).^[19]

Calibration and measurement capability (CMC)

Amount of substance, Advanced materials, Japan, NMIJ (National Metrology Institute of Japan)

Expanded uncertainty is shown as the range from the uncertainty for value of minimum quantity to that for value of maximum quantity.

| NMI Service Identifier | Measurement Service Sub-Category | Matrix | Measurand | | Dissemination Range of Measurement Capability | | | Range of Expanded Uncertainties as Disseminated | | | | | |
|------------------------|----------------------------------|-----------|----------------------|---------------|---|-------|-------|---|-----|------|-----------------|---------------------|---|
| | | | Analyte or Component | Quantity | From | To | Unit | From | to | Unit | Coverage factor | Level of confidence | Is the expanded uncertainty a relative one? |
| 8101-1 | Polymers and plastics | ABS resin | cadmium | Mass fraction | 1 | 10000 | mg/kg | 4 | 0.5 | % | 2 | 95 % | Yes |
| 8101-2 | Polymers and plastics | ABS resin | chromium | Mass fraction | 1 | 10000 | mg/kg | 4 | 0.5 | % | 2 | 95 % | Yes |
| 8101-3 | Polymers and plastics | ABS resin | mercury | Mass fraction | 1 | 10000 | mg/kg | 4 | 0.5 | % | 2 | 95 % | Yes |
| 8101-4 | Polymers and plastics | ABS resin | lead | Mass fraction | 1 | 10000 | mg/kg | 4 | 0.5 | % | 2 | 95 % | Yes |

| Range of Certified Values in Reference Materials | | | Range of Expanded Uncertainties for Certified Values | | | | | | Mechanism(s) for Measurement Service Delivery | Comments |
|--|-------|-------|--|-----|------|-----------------|---------------------|---|---|--|
| From | To | Unit | From | To | Unit | Coverage factor | Level of confidence | Is the expanded uncertainty a relative one? | | |
| 1 | 10000 | mg/kg | 4 | 0.5 | % | 2 | 95 % | Yes | NMIJ CRM 8102-a, 8103-a, 8105-a, 8106-a, 8112-a, 8113-a, 8115-a, 8116-a | Pellet and disk forms Approved on 19 June 2014 |
| 1 | 10000 | mg/kg | 4 | 0.5 | % | 2 | 95 % | Yes | NMIJ CRM 8102-a, 8103-a, 8105-a, 8106-a, 8112-a, 8113-a, 8115-a, 8116-a | Pellet and disk forms Approved on 19 June 2014 |
| 1 | 10000 | mg/kg | 4 | 0.5 | % | 2 | 95 % | Yes | NMIJ CRM 8112-a, 8113-a, 8115-a, 8116-a | Pellet and disk forms Approved on 19 June 2014 |
| 1 | 10000 | mg/kg | 4 | 0.5 | % | 2 | 95 % | Yes | NMIJ CRM 8102-a, 8103-a, 8105-a, 8106-a, 8112-a, 8113-a, 8115-a, 8116-a | Pellet and disk forms Approved on 19 June 2014 |

Key Comparison Database (KCDB) of the International Bureau of Weights and Measures (BIPM) (July 2014)^[11]

Fig. 6 Example of the CMC registration to KCDB (plastics for heavy metal analysis)

from overseas as well as inside Japan is large, and 18 % of the number of the heavy metal analysis CRMs and 12 % of the number of the brominated flame retardant analysis CRMs have been disseminated to the customers overseas.

5.2 Monitoring of the stability and extension of the expiration date

For NMIJ's plastic CRMs, stability monitoring is conducted after the start of dissemination, following the stability test⁽²⁰⁾ during its development. Although in general, CRM is given an expiration date on its certificate, the expiration date may be extended based on the stability monitoring, and many have been extended as shown in Fig. 9. However, there is one example which unfortunately failed, and this must be reported here.

In the stability monitoring for NMIJ CRM 8113-a and NMIJ CRM 8116-a (four metals, high concentration, ABS), concentration changes were observed beyond the expanded uncertainties. First, measurement mistake was suspected, but it was finally found that there was increased oxygen in the ABS matrix. We had to correct the property values by sailing up the time, and this caused inconveniences to the users. The

drying condition was thoroughly considered and established during the development. The change in property value did not occur in the corresponding low concentration CRMs (NMIJ CRM 8112-a and NMIJ CRM 8115-a), was not seen in the other plastic CRMs, and was a phenomenon observed in the high concentration CRM containing Hg. It was concluded that the oxygen was taken in the matrix in some form, and the concentration of heavy metal decreased due to the increased mass of the matrix. It is assessed that this increase has been basically ceased at this moment. The details will be published elsewhere.

5.3 Prospect for the related CRM in the future

In the field of RM development in response to the hazardous substance regulation, other than the plastics presented in the present paper, there are CRM developments of lead-free solder (chip), phthalate-ester-containing plastics, bisphenol-A-containing plastics, and plastic (PP) for bromine analysis. Currently, consideration is being made for glass CRMs.

In the RoHS directive, there was no description on the addition of substances subject to regulations, but there is a possibility of addition in the new RoHS directive.



Fig. 7 Examples of the NMIJ CRMs in response to the RoHS directive

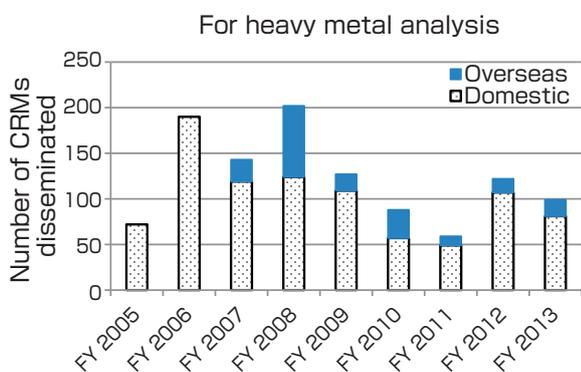


Fig. 8-a Annual change of the total dissemination number of CRMs for heavy metal analysis

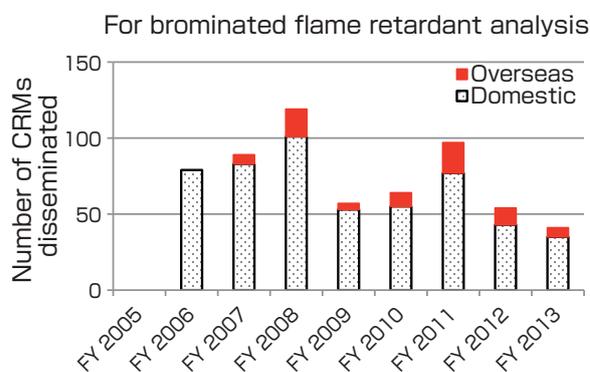


Fig. 8-b Annual change of the total dissemination number of CRMs for brominated flame retardant analysis

In the future, for brominated flame retardants, we will produce a PS CRMs containing 100 ppm each of DBDE, hexabromocyclododecane (HBCDD, a candidate for addition as target substance of the new RoHS directive), and tetrabromobisphenol-A (TBBPA). Other than those, we are in the process of producing CRMs of phthalate-ester-containing PVC and bisphenol-A-containing polycarbonate.

The development of plastic CRMs in response to the RoHS directive was started due to strong demand from industry. However, for the general demand of metrological standards including reference materials, daily information is obtained through various channels such as the NMIJ Metrology Club and NMIJ seminars. Systematic surveys are also conducted, as exemplified by the large-scale demand survey conducted by the Measurement and Intellectual Infrastructure Division, METI in the early 2013, and NMIJ participated to play a central role. The survey results and the developing plan for standards are presented as the “New developing plan of metrological standards and specific promotion of their use”^[21] on the METI website. NMIJ must engage in this plan with limited human and material resources; therefore, deciding what to focus on is extremely important. We hope NMIJ would be able to catch the social demand from the information including the above survey and be able to respond promptly.

6 Conclusion

For the NMIJ CRMs, the developments in the relatively

early stage and the current situation are described in detail in References [22] and [23]. How should the world respond to similar cases which may occur again some time in the future with the enforcement of the RoHS directive? Although the priority on ideal which tends to occur in the EU is understandable, discussions must include the CRMs which may become necessary in the enforcement of regulations. Ideally, someone who knows the actual manufacturing process should join the stages of regulation drafting and the document standards necessary to follow the regulation should be created concurrently. Japan was able to respond relatively quickly to the RoHS directive, but it is also a fact that much confusion occurred in industry. The RoHS directive is an EU directive and is just a domestic law, but it has major impact around the world. Therefore, it should be open to the world. For the perspective of the risk of brominated flame retardants, it is also necessary to pay attention to the differences in sense of values, such as whether one fears the bioaccumulation of substances or the fire which may occur because the flame retardant is not used.

When various regulations are issued in various countries, how NMIJ as a metrology institute should respond will be an issue in the future. Although not all issues can be dealt with, NMIJ must capture such actions as quickly as possible and start response activities if there are CRMs which must be newly developed, through collaboration with the stakeholders in industry and others.

| CRM No. | Resin type | Level | Cd | Cr | Pb | Hg | DBDE | Form | 04 | 05 | 06 | 07 | 08 | 09 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
|------------|------------|-------|----|----|----|----|------|--------|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 8102-a | ABS | Low | ⊙ | ⊙ | ⊙ | | | Pellet | ■ | → | → | → | → | ● | → | → | → | → | ● | → | → |
| 8103-a | ABS | High | ⊙ | ⊙ | ⊙ | | | Pellet | ■ | → | → | → | → | ● | → | → | → | → | ● | → | → |
| 8105-a | ABS | Low | ⊙ | ⊙ | ⊙ | | | Disk | | ■ | → | → | → | ● | → | → | → | → | ● | → | → |
| 8106-a | ABS | High | ⊙ | ⊙ | ⊙ | | | Disk | | ■ | → | → | → | ● | → | → | → | → | × | | |
| 8112-a | ABS | Low | ⊙ | ⊙ | ⊙ | ⊙ | | Pellet | | | ■ | → | → | → | → | ● | → | → | → | → | → |
| 8113-a(02) | ABS | High | ⊙ | ⊙ | ⊙ | ○ | | Pellet | | ■ | → | → | → | → | △ | □ | ● | → | → | → | → |
| 8115-a | ABS | Low | ⊙ | ⊙ | ⊙ | ⊙ | | Disk | | | ■ | → | → | → | → | ● | → | → | → | → | → |
| 8116-a(02) | ABS | High | ⊙ | ⊙ | ⊙ | ○ | | Disk | | | ■ | → | → | → | △ | □ | ● | → | → | → | → |
| 8123-a | PVC | High | ⊙ | ⊙ | ⊙ | ⊙ | | Pellet | | | | | ■ | → | → | → | → | → | ● | → | → |
| 8133-a | PP | High | ⊙ | ⊙ | ⊙ | ⊙ | | Pellet | | | | | ■ | → | → | → | → | → | ● | → | → |
| 8136-a | PP | High | ⊙ | ⊙ | ⊙ | ⊙ | | Disk | | | | | ■ | → | → | → | → | → | ● | → | → |
| 8108-a | PS | | | | | | ⊙ | Disk | | | ■ | → | → | → | × | | | | | | |
| 8108-b | PS | | | | | | ⊙ | Disk | | | | | | ■ | → | → | → | → | → | ● | → |
| 8109-a | PVC | | | | | | ⊙ | Disk | | | | | | ■ | → | → | → | → | ● | → | → |
| 8110-a | PS | | | | | | ⊙ | Disk | | | | | ■ | → | → | → | → | → | ● | → | → |

⊙: Certified value, ○: Indicative value

■: Development, ●: Extension of expiration date, △: Change of certified value, □: Recertification,

×: Sold out (Year of development is fiscal year in the western calendar; years of the others are western calendar years.)

Fig. 9 Year of development and status of extension, and so on

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Discussions with Reviewers

1 Overall

Comment (Koichi Chiba, AIST)

This paper provides an appropriate description of the social background where the plastic CRMs were demanded, the process from capturing the demand to developing the CRMs, the technological developments to satisfy the demand, and the current status of dissemination of certified reference materials as contribution to society. It has an interesting content which illustrates the course whereby the R&D at AIST becomes a fruit in society.

Comment (Shigeko Togashi, AIST)

This paper describes the strategy and process by which the internationally recognized CRMs for analysis of heavy metals and brominated flame retardants were developed, in prompt response to the strong demand from industry for immediate action coping with the RoHS directive. It is a theme appropriate for a paper in *Synthesiology*.

2 Addition of the research scenario diagram

Comment (Shigeko Togashi)

For the research scenario in chapter 2, please show a diagram of the scenario followed for the achievement of the objective, based on the research potential up to that point. To be of use as a reference to other R&Ds, please create a framework of the scenario which can be generalized, and describe the specific strategies for the issues you encountered.

Answer (Akiharu Hioki)

As you indicated, I created the diagram of the research scenario in chapter 2.

3 CRM

Question (Shigeko Togashi)

NMIJ distributes many CRMs other than the CRMs mentioned in the present study. What are the common and different points among the CRMs in the present paper and the other CRMs?

Answer (Akiharu Hioki)

The CRMs can be roughly divided into ones for calibration and the others for validation. The CRMs in the present study were mainly developed for the latter purpose. The NMIJ CRMs are produced based on NMIJ's management system in compliance with the ISO/IEC17025 and ISO Guide 34, and the basic idea for the manufacturing process and for determining the certified values for CRMs in the present study is the same as for the other NMIJ CRMs for validation. On the other hand, the CRMs in the present study were quickly designed and developed in response to the demand which arose around the world, although those were for extremely limited use (response to the RoHS directive). They are discriminated from the other CRMs by the fact that timely distribution was possible. Our CRMs became one of the global bestsellers, and are distributed widely around the world.

Development of forging process for magnesium alloy continuous cast bars

— Forging process utilizing grain refinement —

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[Translation from *Synthesiology*, Vol.8, No.1, p.41-52 (2015)]

Reducing resource consumption and carbon dioxide emission are recognized as urgent issues. One way of addressing these issues is to reduce product weight. Magnesium alloys are considered promising candidates because of their lightness. To manufacture products using magnesium alloys, we require forging technology that afford higher size accuracy and strength. This paper introduces the results of joint research with a company for the development of a new forging process for magnesium alloys continuous cast bars. We describe the research background, goals of the project, fundamental technologies employed to address these goals, and the integrative/synthetic process.

Keywords : Magnesium alloy, continuous cast bars, forging, dynamic recrystallization, grain refinement, heat sink

1 Introduction

Against a background of social demand for energy and resource saving, the weight reduction and recycling promotion are issues in a wide range of industrial products from transportation machines to home appliances. Magnesium is the lightest material among the structural metallic materials and is readily recyclable. Therefore, its application to various industries including vehicles is expected. However, it is not widely used compared to the aluminum alloy at this point, one of the reasons being that the magnesium alloy parts are expensive. Table 1 shows the comparison of the magnesium alloy and aluminum alloy for the forged parts that are the subjects of this research. There are not many differences in the material properties between the aluminum and magnesium alloys. However, in terms of the cost of material, magnesium alloy is five to six times more expensive than the aluminum alloy. Also, magnesium alloy has poor plastic deformability, so that only hot forging can be done. In contrast to magnesium alloy, the aluminum alloy can be forged at lower temperatures (warm and cold forging). Therefore, the power consumption for processing is higher for forging magnesium alloy. Due to the above factors, the cost of magnesium alloy forged products is six to seven times more than the cost of aluminum alloy forged products. However, forging is a plastic forming process that allows the manufacture of high quality parts at high productivity. Therefore, the industry is seeking the establishment of the forging technology for magnesium alloy and the cost reduction of the magnesium alloy forged parts.

AIST aimed for the manufacture of magnesium forged parts with low cost and high reliability, jointly with the Sokeizai Center, in the “Project for the Development of Magnesium Forged Parts Technology” supported by the New Energy and Industrial Technology Development Organization (NEDO) for the fiscal years 2006 to 2010. After the completion of the Project, joint research was done with the Miyamotokogyo Co., Ltd. to continue development toward practical realization of the newly developed technology.

2 Background of the development of forging technology for magnesium alloy continuous cast bars^[1]

In this chapter, we discuss the situation of magnesium alloy forging in 2006, and the goals set for the development of forging technology for magnesium alloy continuous cast bars in the NEDO Project.

2.1 Situation of the magnesium forging process

In the NEDO Project, to clarify the issues in the development of magnesium alloy forging technology, we conducted prototype forging and evaluated the actual parts made by a commercial process using a general-use mechanical press, with the actual magnesium alloy extruded material as forging material. As a result, it was found that in the prototype forged parts, the grain size was coarse since they were forged at high temperature of about 400 °C, and this prevented the improvement of the mechanical properties of forming that is expected for forged parts. That is, in 2006, there was

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Table 1. Comparison of the magnesium alloy forging material and aluminum alloy forging material

| | | | Magnesium alloy (AM60) | Aluminum alloy (A6061) |
|---------------|------------------------|---|-------------------------------|-------------------------------|
| Material | Specific gravity | | 1.74 (pure Mg) | 2.70 (pure Al) |
| | Material, structure | Material | Extruded material | Extruded material |
| | | Grain size | 20 ~ 50 μm | 20 ~ 50 μm |
| | Property | Strength | 260 MPa | 280 MPa |
| | | Elongation | 10 % | 12 % |
| Drawing ratio | | 35 % | 45 % | |
| Process | Weight reduction rate* | Thinning, downscaling | Weight reduction 30 % or more | Weight reduction 20 % or more |
| | Forging, forming | Forming method | Hot process only | Cold and hot processes |
| | Size accuracy | During hot process | ±1.5 ~ 2.0 mm | ±1.0 ~ 1.5 mm |
| Cost | Material | Comparison with current product (extruded material) | 500 ~ 600 | 100 |
| | Product | Finished forged product | 600 ~ 700 | 100 |

Here, the examples shown are for the AM60 (Mg-6 mass% Al -0.1 mass% Mn) magnesium alloy and the A6061 (Al-0.8 mass% Mg-0.7 mass% Si) aluminum alloy that are representative forging materials.

*Here, weight reduction rate is the weight reduction achieved by replacing the small automobile parts such as the iron structural support material with aluminum or magnesium alloy materials.

insufficient improvement of the properties of the forged product itself, because importance was placed on the forming technique without defects or cracks for the magnesium alloy forging.

2.2 Goal setting for the forging technology development

For the popularization of the magnesium alloy forged parts, direct forging from low-cost cast material is desired instead of extruded material. Also, the improvement of mechanical property by forging must be realized. Therefore, in the NEDO Project, the R&D topics for magnesium alloy forging were set as follows and the R&Ds were started: 1) the investigation of forgeability of low-cost materials (continuous cast bars), 2) the development of forging process for continuous cast bars, 3) the achievement of forging at temperatures lower than 400 °C (suppression of grain size coarsening in forged parts), and 4) the achievement of improved mechanical property of parts by forging (by controlling the grain roughness in forged parts).

Figure 1 shows the estimate of cost reduction expected by using magnesium alloy continuous cast bars as forging material. When the forged parts are manufactured using the magnesium alloy continuous cast bars, it is expected that the price of the forged parts will fall to about one-fourth of the current price because there is no extrusion process.

3 Increasing the formability of magnesium alloy continuous cast bars^[1]

3.1 Investigation of the solution methods based on conventional knowledge

The point of this R&D is to increase the formability of forging material and to increase the strength of forged parts. While the magnesium alloy forging is a process in which the materials are deformed at elevated temperature, it is known that the deformation of metallic materials is dominated by grain boundary sliding at elevated temperature.^[2] Also, since the stress for grain boundary sliding decreases as the grain size becomes smaller, deformation occurs readily at elevated temperature as the grain size of the material becomes smaller.^[2] On the other hand, the phenomenon where the yield stress of the metallic material at room temperature increases as the grain becomes smaller is known as the Hall-Petch relation.^{[3]-[5]} From the above knowledge, we thought the reductions of grain size of the forging materials and forged parts were important in solving the issue.

It is known that when the metallic material is deformed at elevated temperature, new grains are generated due to dynamic recrystallization, and the initial grains disappear.^[6] Also, it is reported that magnesium alloys readily undergo dynamic recrystallization, and grain refinement can be achieved relatively easily.^[7] Therefore, we started the R&D by investigating the grain refinement behavior by dynamic recrystallization of the magnesium alloy continuous cast bars.

3.2 Investigation of the dynamic recrystallization behavior of magnesium alloy continuous cast bars

In this chapter, we explain the result of investigating the grain refinement behavior by dynamic recrystallization of the magnesium alloy continuous cast bars, in the NEDO Project led by AIST to obtain the basic knowledge for the development of forging technology.

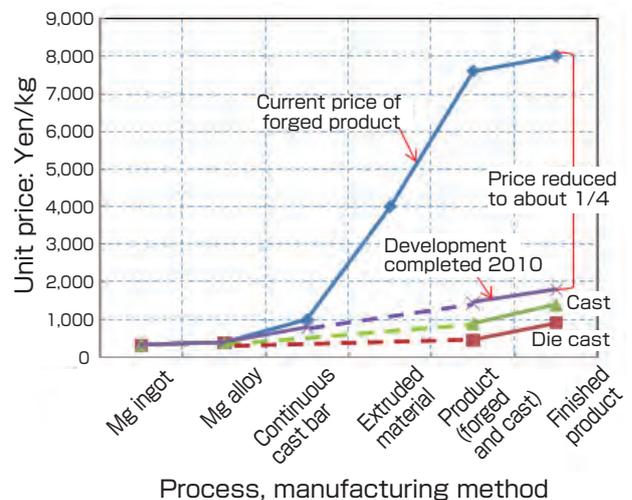


Fig. 1 Cost estimate of the magnesium alloy parts

3.2.1 High-temperature compression test of the AZ91 alloy continuous cast bar

We conducted a high-temperature compression test at AIST, using the homogenized (heated at 410 °C for 24 h) AZ91 (Mg-9 mass% Al-1 mass% Zn) magnesium alloy continuous cast bar (made by Sankyo Tateyama, Inc.). As a representative example, the test samples of 10 mm diameter and 12 mm height were compressed to 80 % at three different temperatures (250 °C, 300 °C, and 330 °C) and strain rates (0.01 s⁻¹, 0.1 s⁻¹, and 1 s⁻¹). The obtained microstructures (grain size) are shown in Fig. 2. From this result, it was found that the grain size could be relatively easily refined to 10 μm or less when the AZ91 magnesium alloy continuous cast bar was compressed and deformed at 300 °C or less.

3.2.2 Upset compression test of the AZ91 magnesium alloy continuous cast bar

Next, we conducted the upset compression test for the scale-up AZ91 alloy sample pieces (40 mm diameter, 48 mm height), using the servo press owned by Miyamotokogyo Co., Ltd. to investigate the effect of reduction ratio and compression speed on the grain refinement behavior. Figure 3 shows the variation in grain size as a function of the reduction ratio when deformation was done at 200 mm/s. The grain became finer at high reduction ratio, but cracks occurred on the side of the sample at reduction ratio of 60 %. Figure 4 shows the variation in grain size as a function of the processing temperature when the deformation was carried out at reduction ratio of 40 %. Although the grains became finer as the temperature decreased, there was no dependency on deformation speed of the grain diameter at 300 °C. From the above results, it was found that the grain diameter of AZ91 magnesium alloy continuous cast bar could be refined to about 10 μm without cracking, if the deformation of 30~40 % was done at 300 °C.

4 Prototype forging of the magnesium alloy

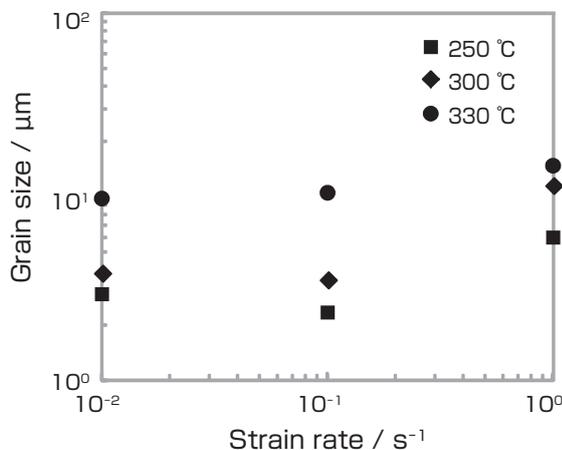


Fig. 2 Grain size of AZ91 (Mg-9 mass% Al-1 mass% Zn) magnesium alloy continuous cast bar after high-temperature compression (reduction ratio : 80 %)

continuous cast bar and investigation for achieving high strength in forged parts^[1]

In this chapter, we explain the outline of the forging technology for magnesium alloy continuous cast bars developed by AIST based on the research results obtained in the NEDO Project as explained in the previous chapter, and the prototype forging at AIST using the developed technology.

From the experimental results of the dynamic recrystallization behavior of the magnesium alloy continuous cast bars, AIST proposed a forging process shown in Fig. 5. In this process, the compression process of 30~40 % was applied at 300 °C to the magnesium alloy continuous cast bar to refine the grain size to about 10 μm in the first half of the process. The forging material, hence, is expected to change into a material with good formability due to grain refinement. In the latter half of the process, the forging process was continued until the final form was achieved.

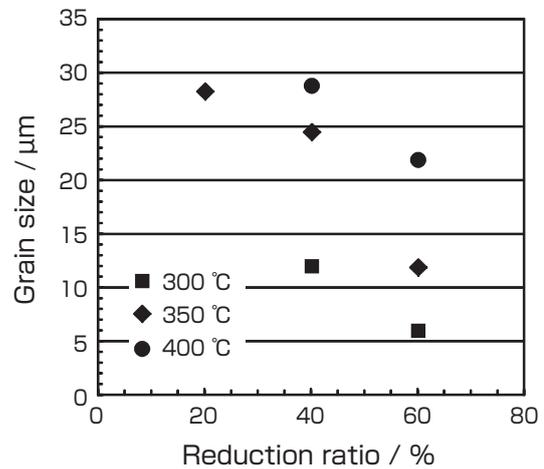


Fig. 3 Variation in grain size as a function of the reduction ratio for AZ91 (Mg-9 mass% Al-1 mass% Zn) magnesium alloy continuous cast bar (deformation speed: 200 mm/s)

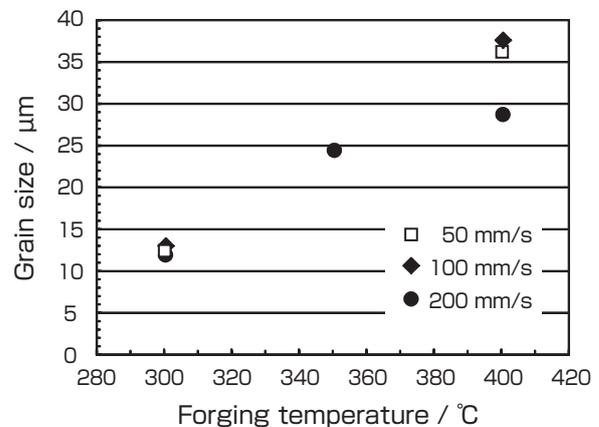


Fig. 4 Variation in grain size as a function of the processing temperature for AZ91 (Mg-9 mass% Al-1 mass% Zn) magnesium alloy continuous cast bar (reduction ratio : 40 %)

As mentioned in the previous chapter, the dynamically recrystallized microstructure of magnesium alloy is dependent on the processing temperature and strain rate.^[8] Therefore, to achieve the process set as the goal, the servo press was useful since the processing speed and sliding position could be controlled arbitrarily. The prototype forging was conducted using the servo press at AIST, and the adequacy of the aforementioned forging process was investigated.

Figure 6 shows the forging process using the servo press conducted at AIST. The preheated forging materials (blanks) were placed in the heated mold, and compression was applied from above by a punch process. Since the diameter of the blanks is smaller than the diameter of the mold, the blanks spread sideways at first, and the diameters of the blanks and mold match at a certain point. The so-called upset

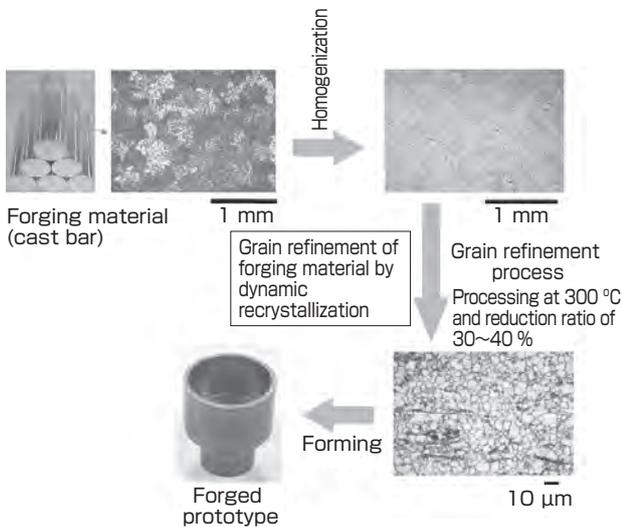


Fig. 5 Outline of the forging process for magnesium alloy continuous cast bar

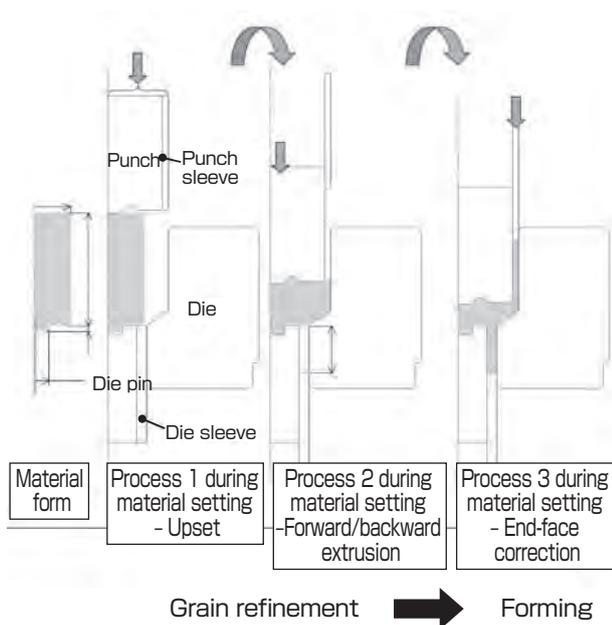


Fig. 6 Forging process using the servo press

compression process (reduction ratio of about 40 %) to this point is the process of grain refinement. When the material is pressed further with the punch, it is pushed out both forward and backward, and formed into its final form. This process is done in one step, but the first half is the grain refinement process, while the latter is the forming process.

Figure 7 is the photograph of the exterior appearance of the forged product (material is AZ91 magnesium alloy) created as the first prototype in this process. In the photograph, 1 is the part by backward extrusion, 2 is the part by upset forging, and 3 is the part by forward extrusion. AIST conducted about 150 prototype forging with varied temperatures, processing speed, and cooling speed of the forged product, and the results of the microstructural observation and the tensile test were organized into a database. The forged prototype shown in Fig. 7 was forged at 300 °C and forging speed of 10 mm/s, and there were no defects observed. It was confirmed that forward/backward tube extrusion forging with area reduction rate of 81 % was possible at 300 °C using the new forging process for magnesium alloy continuous cast bars proposed by AIST. This result was evaluated highly by the evaluation committee members in the follow-up evaluation of the Project. When the microstructure of the prototype formed parts was observed, the grain size was refined to 10 μm or less in the forwardly extruded, the upset forged, and backwardly extruded parts. As for the mechanical properties of the upset forged section, tensile strength at room temperature was 359 MPa and breaking elongation was 19 %. This tensile property was higher than that of the original material (226 MPa, 15 %), and the increased mechanical property by forming as expected for forged parts was realized. In conclusion, we achieved the goals that were initially set.

5 Investigation of the realization of the forging process for magnesium alloy continuous cast bars

5.1 Goals set in the realization research

We succeeded in forging the magnesium alloy continuous cast bar at 300 °C that was about 100 °C lower than the conventional method at the prototype level, using the

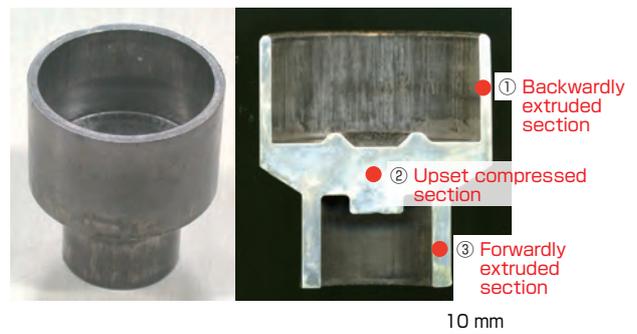


Fig. 7 Example of the forged prototype (Material: AZ91 magnesium alloy continuous cast bar)

Table 2. Decrease of the processing cost expected by lowered forging temperature

| | Conventional process | New process (low-temperature forging) |
|-------------------|----------------------|---------------------------------------|
| Material | 100 | 100 |
| Consumed power | 100 | 70 |
| Post treatment※1 | 100 | 50 |
| Post processing※2 | 100 | 98 |
| Total cost | 100 | 70 |

※1 : Mainly cleansing of forged products such as removal of lubricants

※2 : Post processing such as cutting and alumite treatment

process developed in the NEDO Project. As the next step after the completion of the Project, AIST held thorough discussions on the results of the aforementioned NEDO Project with Miyamotokogyo, from the perspective of applying them to actual practice. As a result, we were able to share the recognition that it was important to set the goal of developing forging technology to obtain high-strength, high-accuracy formed products at temperatures less than 200 °C, and that the grain refinement was necessary to accomplish this. Setting these two as common goals, AIST and Miyamotokogyo conducted joint research. In the course of discussion, Miyamotokogyo proposed the following points for the processing cost, environmental measures, and workplace environment, as merits of low-temperature forging.

1) Processing cost: in hot forging where the temperatures are 300 °C or more, special furnace to heat the forging material is necessary. In contrast, when forging at temperatures of 200 °C or less, heating can be done sufficiently by an infrared heater or a hot plate. Also, since the product accuracy increases at low temperature, it is expected to reduce the number of steps and reduce the cost of cutting. Moreover, the amount of power needed to maintain the heat of the material and mold can be reduced, and the lifespan of the mold can be increased. Considering the above points, the expected decrease in processing cost by low-temperature forging is shown in Table 2. It is thought that the cost reduction in power consumption and after-treatment will be large, and it is estimated that the total processing cost will be 20~30 % less than the conventional processing method.

2) Environmental measures: In forging at temperatures of 200 °C or less, water-soluble lubricant that can be more readily removed compared to graphite solid lubricants can be used. While the graphite lubricants have low cost with high lubrication property, there is the danger of fire since the flash point of the base oil used to disperse the graphite is 170~200 °C. Also, the possibility that the contamination of the work environment by graphite may cause health damage to human beings has been indicated. Therefore, the workplace contamination in the lubrication process is expected to

decrease by using the water-soluble lubricants.

3) Work environment: In the case of hot forging, the workers must wear special equipment to protect against burns, and the companies must pay extra allowance to workers for exposure to heat. In contrast, the materials can be handled without using special equipment if the forging temperature is 200 °C or less. That is, the work environment is expected to improve compared to hot forging.

5.2 Consideration of the solutions based on knowledge obtained in the research so far

In the “Project for the Development of Technology for Magnesium Forged Parts,” it was not possible to decrease the temperature only of the forming process as forging was done in one step using a single mold. Therefore, this time, we tried the two-step forging where the grain refinement and forming processes were separated. The outline of the considered forging process is shown in Fig. 8. In this forging process, the processes of grain refinement and forming are separated into two steps. That is, the material is processed by upset compression at a certain temperature and at a certain compression rate, and the grain size is refined to about 10 μm by dynamic recrystallization. The samples are removed and the forging is done at 200 °C or less. AIST has high potential for the microstructural control and analysis technologies for metallic materials, while Miyamotokogyo is a manufacturer with high potential for the forging process and peripheral technologies (mold, lubrication, etc.). Therefore, the individual potential was utilized to consider and investigate the processes in the following steps.

5.2.1 Analysis of the grain refinement behavior in the forging material

To check the occurrence of grain refinement by dynamic recrystallization, the upset compression test was conducted at AIST for the forging material using a servo press.

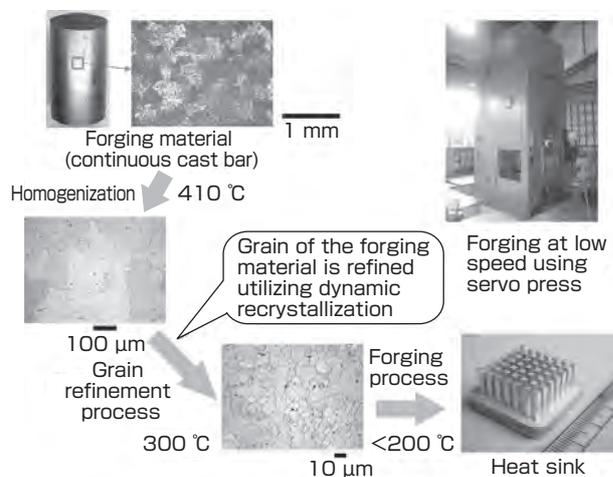


Fig. 8 Outline of the developed low-temperature forging process

The non-combustible magnesium alloys, where Ca was added to the AZ91 magnesium alloy to increase the flash point temperature to 200~300 °C, were used as the forging material.^[9] The amounts of Ca added were 0.2 mass%, 0.4 mass%, 0.6 mass%, and 1.0 mass%. The samples underwent 24-hour heat treatment (homogenization) at 410 °C before the test. The sample size was 25 mm in diameter and 30 mm in height. Figure 9 shows an example of the measurement results of grain size for the material compressed at 350 °C and 1 mm/s. While the grain size of the original material was 100~200 μm, the grain size after upset compression at 350 °C to 60 % was 10 μm for all alloys. The grains were refined to one-tenth or less. In case of 1.0 mass% Ca added alloy, the grain size was stabilized at about 8 μm when the reduction ratio was 60 % or more.

5.2.2 Evaluation of the compression deformation property of the grain-refined material

To investigate the forgeability at 200 °C or less, a high-temperature compression test of the grain-refined materials was conducted, and the compression deformation behavior was investigated at AIST.

Figure 10 shows the results of the compression test conducted for the magnesium alloy sample of 0.2 mass% Ca added AZ91 at temperatures of 200 °C, 175 °C, and 150 °C and initial strain rate of $4.2 \times 10^{-3} \text{ s}^{-1}$, in which the samples were compressed to 60 % at 350 °C and 1 mm/s. The size of sample pieces was 8 mm in diameter and 12 mm in height. The reduction ratio where breakage occurred were about 16 % at 150 °C, about 20 % at 175 °C, and about 30 % at 200 °C. The result that 16 % deformation was possible at 150 °C indicates that forging at 200 °C or less may be possible if the grain size of the material is refined to about 10 μm.

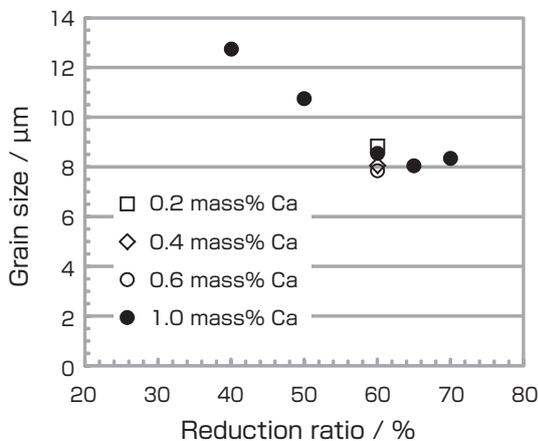


Fig. 9 Grain size after high-temperature compression of AZX91 + 0.2 mass% Ca, 0.4 mass% Ca, 0.6 mass% Ca, 1.0 mass% Ca alloy continuous cast bars (temperature: 350 °C, processing speed:1 mm/s)

5.2.3 Consideration of the possibility of low-temperature forging

Based on the data obtained in the previous section, AIST and Miyamotokogyo discussed the possibility of low-temperature forging. As a result, it was judged that forging at 200 °C or less might be possible by refining the grain of the material to about 10 μm. It was decided that prototype forging would be conducted. For the prototype forged part, the square pin heat sink was selected since Miyamotokogyo had the experience of forging it from aluminum alloys. The basic structure of the square pin heat sink was of 30 mm angle × 3.5 mm thickness, and the square pin part was of 2 mm angle × 8 mm height. There were 49 pins.

5.2.4 Grain refinement of the forging material

Next, upset compression was done using the servo press at Miyamotokogyo for grain refinement of the forging material. The microstructural observation was done for the material that underwent upset compression, and the grain refinement behavior was studied at AIST.

The two types of magnesium alloys used for forging were commercially available AZ31 (Mg-3 mass% Al-1 mass% Zn) magnesium alloy continuous cast bar (155 mm diameter) and AZ61 (Mg-6 mass% Al-1 mass% Zn) magnesium alloy continuous cast bar (55 mm diameter). Both were homogenized for 24 hours at 410 °C. In the grain refinement process, the blank materials with average grain size of 100 μm or more were upset to a specified compression rate at temperature of 300 °C. From the perspectives of promoting the dynamic recrystallization and preventing the cracks in the blanks in the initial process, upsetting was done at relatively slow speed of average 5~10 mm/s. Although there were some regions where the grain diameter was about 10~20 μm in the AZ31 magnesium alloy continuous cast bar, refinement progressed to grain size of 5 μm or less by dynamic recrystallization. On the other hand, while dynamic recrystallization occurred in the AZ61 magnesium alloy continuous cast bar, the average grain size was 10 μm. Thus the grain refinement of the forging material by the upset compression process was confirmed.

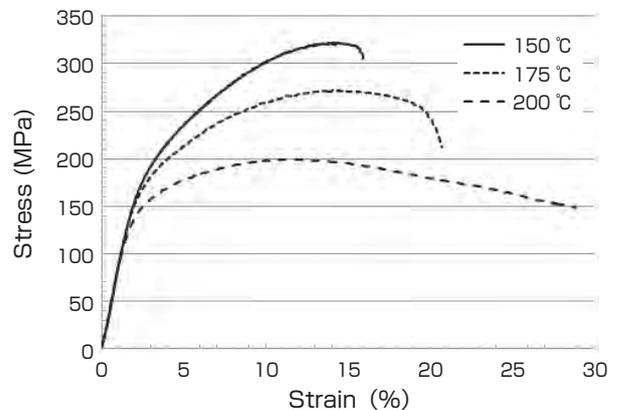


Fig. 10 Result of the compression test of AZX91 + 0.2 mass% Ca alloy that underwent grain refinement

Table 3. Comparison of the development goal of this research and conventional technology

| | | | Magnesium alloy (AM60) | Magnesium alloy (Development goal value) | Aluminum alloy (A6061) |
|----------|-----------------------|---------------------------------|--|--|--|
| Material | Material, structure | Material | Extruded material | Continuous cast bar | Extruded material |
| | | Grain size | 20 ~ 50 μm | 10 μm (after grain refinement) | 20 ~ 50 μm |
| | Property | Strength | 260 MPa | 340 MPa | 280 MPa |
| | | Elongation | 10 % | 15 % | 12 % |
| | | Drawing rate | 35 % | 60 % | 45 % |
| Process | Weight reduction rate | Thinning, downscaling | Weight reduction 30 % or more | Weight reduction 30 % or more | Weight reduction 20 % or more |
| | Forging, forming | Forming method | Hot process only | Warm process possible | Cold and hot process |
| | Size accuracy | | $\pm 1.5 \sim 2.0 \text{ mm}$ (during hot process) | $\pm 0.3 \text{ mm}$ (during warm process) | $\pm 1.0 \sim 1.5 \text{ mm}$ (during hot process) |
| Cost | Material | Comparison with current product | 500 ~ 600 | 120 ~ 140 | 100 |
| | Product | Finished forged product | 600 ~ 700 | 150 | 100 |

*Development goal values of the research were added to Table 1.

5.2.5 Prototype forging as a forming process of grain-refined material

Since grain refinement was confirmed for the forging material, we conducted prototype forging using the servo press at Miyamotokogyo. The manufactured prototype was subject to exterior evaluation at Miyamotokogyo and microstructure evaluation at AIST.

Figure 11 shows a photograph of the heat sink manufactured by the developed forging method using the AZ31 magnesium alloy continuous cast bar to which grain refinement treatment was done. The materials that underwent grain refinement treatment were used as blanks, and forging was done at temperatures 100 °C, 150 °C, and 200 °C. The average extrusion ratio was 4.6, average extrusion strain was 1.5, and reduction of area was 0.78. To prevent cracking of the material, forging was done at relatively slow speed of average 5~10 mm/s. There were no cracks at all forging temperatures, and a robust heat sink with 49 pins of even height was forged. Similar heat sinks were manufactured by the new forging method, using the AZ61 magnesium alloy continuous cast

bars. Heat sink is a part for which mechanical strength is not required. However, from microstructural observation, it was confirmed that the grain diameter of the square pin section was refined to 10 μm or less. Therefore, it is thought that it would have sufficient mechanical strength.

5.2.6 Investigation of the adequacy of our forging process and the magnesium alloy forged prototype

After the completion of the prototype forging, the adequacy of the forging process was verified at Miyamotokogyo and AIST.

In the prototype forging, it was confirmed that the forging of magnesium alloy with relatively complex form was possible at 200 °C or less, by controlling the grain size to about 10 μm or less. With the AZ61 alloy that has inferior forgeability compared to the AZ31 alloy, forging was possible without any problem if the grain was refined by dynamic recrystallization. From the above results, it is thought that this forging process can be put into practical use.

Also, when the research results are compared with those of

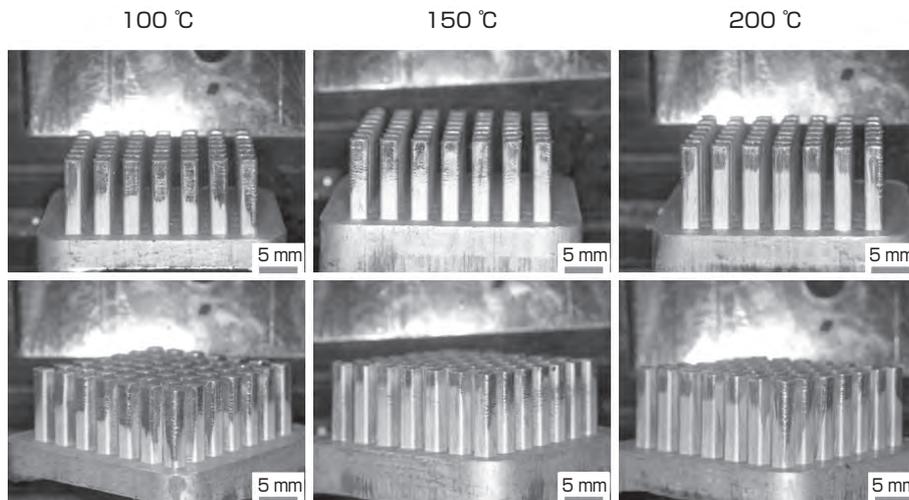


Fig. 11 Appearance of the prototype heat sink (material is AZ31 alloy)

aluminum alloy forged parts as shown in Table 3, although it is about 1.5 times the aluminum alloy in product price ratio, the price is expected to decrease to about one-fourth of the current magnesium alloy forged parts. Although further product cost reduction will be the issue in the future, practical use of magnesium alloy forged parts is now on the horizon for uses where demand for weight reduction is large.

6 Integration of the elemental technologies in this R&D

The development of low-temperature forging technology of the magnesium alloy continuous cast bar was possible by integrating the capabilities of AIST and Miyamotokogyo. Based on the contents and discussions presented up to chapter 5, Fig. 12 summarizes how the hypotheses and elemental technologies that were set in the NEDO Project and joint research to solve the problems were integrated, how the two institutions divided or joined the tasks, and how they were able to achieve the development of the final magnesium alloy forging process and the forged product.

AIST has potential for the microstructural control, analysis, and evaluation technologies of the metallic materials. The point of the low-temperature forging technology of the magnesium alloy continuous cast bar is the refinement of grain size of the material before forging the material into its final form. Therefore, AIST engaged in the analysis of grain refinement behavior by dynamic recrystallization of the forging material, and the analysis of deformation behavior of the grain-refined material at low temperature. Then, based on the results, the possibility of low-temperature forging was

considered together with Miyamotokogyo.

Miyamotokogyo is an aluminum forging manufacturer with experience in parts used in home appliances, precision machines, personal computers, automobiles, as well as leisure products, and has high potential in forging processes and peripheral technologies (mold, lubrication, etc.). In this R&D, it conducted prototype forging of the actual parts using the developed process by utilizing the basic data provided by AIST. It also engaged in the exterior evaluation of the forged prototypes.

AIST was the main player in the first half of this joint research, while Miyamotokogyo played the main role in the latter half. AIST was in charge of the microstructure analysis of the forged prototypes conducted in the latter half. The R&D was conducted under close collaboration.

7 Evaluation of the results and future prospects

7.1 Evaluation of the results

The result of the joint research for the low-temperature forging of magnesium alloy continuous cast bar was publicized in the AIST press release “Achievement of forging of magnesium alloy at low temperature of 200 °C or less” on May 15, 2013.^[10] Immediately after the press release, we had interview requests from newspapers, and several newspapers carried articles on this research. There were also requests for commentary articles from several magazines, and this contributed to the spread of the results.^{[11]-[13]} Moreover, there were coverages by magazines and articles were written.^[14] There were many responses to this research result and it was

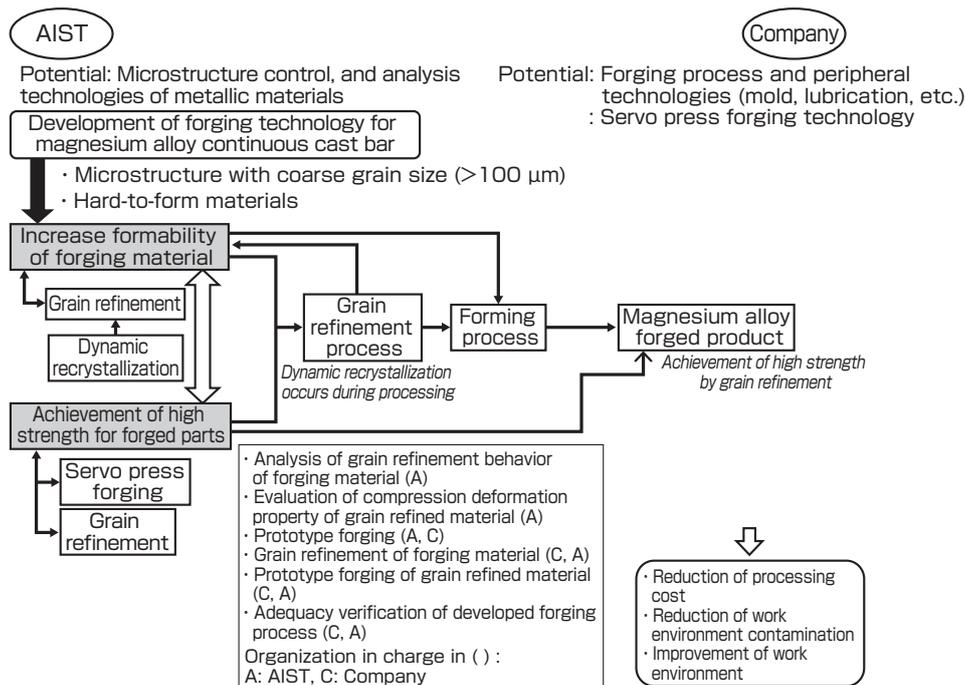


Fig. 12 Integration of elemental technologies in this R&D

highly evaluated.

7.2 Future prospects

Miyamotokogyo is working on decreasing the forging temperature of magnesium alloy and is aiming to achieve cold forging at a region of 100 °C or less. If this is realized, heat maintenance during forging becomes unnecessary, and this is expected to dramatically increase the productivity. Also, lubricants for cold forging can be used, forging accuracy will be increased, and further cost decrease can be expected.

If mass production of magnesium alloy becomes possible in the cold forging region, replacement in the fields where aluminum is currently used or in some fields that use iron may become possible. Application to optics, industrial machines, batteries, power source peripherals, automobiles, motorcycles, and other diverse fields will come into the horizon.

Currently, Miyamotokogyo is seeking new business using the results of this joint research. It has already progressed to mass production of digital camera parts made of low-temperature forged magnesium. Also, it is putting its sales efforts into cable connectors for bullet trains, centrifuge holders, and automobile parts.

8 Conclusion

The development of the forging technology for magnesium alloy continuous cast bars was started as a NEDO project, and continued as joint research with Miyamotokogyo. The point of this R&D was to actively incorporate dynamic recrystallization, which is a phenomenon that has been studied extensively academically, into the manufacturing process, and this enabled the forging of magnesium alloy continuous cast bars that was previously not used as forging material. AIST bridged the basic academic results and the manufacturing process, and we believe this is an example of the practical application of the AIST's slogan "Technology to Society." In the future, we plan to join together the basic core technologies (microstructural control, analysis, and evaluation technologies of materials) of AIST and the manufacturing technologies of the companies through such joint research.

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Discussions with Reviewers

Overall

Comment (Toshimi Shimizu, AIST)

From the perspective of resource and energy saving, there is a social demand for weight reduction in a wide range of industrial products. This paper presents an example of the development of a low-temperature forging process for continuous cast bars that was conventionally considered impossible, using magnesium alloy that has the lightest weight among the structural metal materials. It describes the elemental technologies selected for the development of the forging process that greatly contributes to cost reduction, environmental load decrease, and workplace improvement, as well as its integration scenario, particularly focusing on the close collaboration between AIST's basic core technology and a company's manufacturing technology.

1 Structure of the scenario and elemental technologies

Comment (Toshimi Shimizu)

In the forging of magnesium alloys that has inferior corrosion resistance and plasticity, crystal grain refinement was achieved by actively utilizing the dynamic recrystallization, or changes in the microstructure. Moreover, the story is told of how the difficult low-temperature forging method was developed through joint research with a company using cast bars. However, the first draft seems to be no different from the report of the NEDO Project and the joint research report from the company, and this paper seems to be a mere combination of the two. This means that there is no detailed explanation or description on the details of elemental technologies or the integration scenario that are the essence of a *Synthesiology* paper. Putting it bluntly, it seems you are saying an optimal condition was found when doing investigations using the servo press pertaining to the conditions of major factors (temperature, processing speed, processing rate, etc.) for the dynamic recrystallization that was necessary for refining the grains of the continuous cast bar, and the development was accomplished easily when a company good at cold forging processes gave it a try based on the data you provided them. In your writing, you should present a compelling story including the setting of the social value as the goal, the working hypothesis that you established in doing the research and the verification results, the problems you ran into when integrating with corporate technology, the techniques to overcome them, and the logical development of technological integration, as well as the delineation of importance, difficulty, or urgency of the issues and technologies.

Comment (Akira Kageyama, Research and Innovation Promotion Headquarters, AIST)

When I read the first draft, it seemed that the technological issues and the ways to overcome them were already known, and as a result of patiently doing the experiments, you came up with a forging technology for high-strength magnesium alloy that can be formed at low temperature and is not likely to crack. In reality, I think there must have been parts where the authors' originality was involved in the concept design, hypothesis setting, and combination of the elemental technologies. Therefore, please review the paper by building up the discussion carefully for the processes and results, in line with the direction of *Synthesiology*.

Answer (Naobumi Saito)

I received similar indications from the two reviewers. In the first draft, I provided the description with importance placed on research after the NEDO Project. However, I do not think the readers could understand the meaning of this research unless the process of problem solving in the NEDO Project is described. Therefore, the entire composition of the paper was changed.

2 Integration diagram for the elemental technologies

Comment (Toshimi Shimizu)

I think you need a diagram on the integration and synthesis of the elemental technologies that is absolutely essential for *Synthesiology*. The reviewer added some content and created a rough diagram. It is strictly a proposal, so please use it as a reference only. Please refer to other papers in *Synthesiology* on material development, and do your own adjustment, addition, or correction. Of course, you can create your own original diagram.

Comment (Akira Kageyama)

The following keywords can be picked out from this paper: 1) improvement of mechanical strength, 2) direct forging from cast material, 3) review of manufacturing process of forging material = avoidance of extrusion process, 4) easy formability, 5) dynamic recrystallization, 6) grain refinement, 7) investigation from the perspective of cost reduction, 8) magnesium alloy composition, 9) forming temperature, strain speed, and reduction ratio as process conditions and the introduction of the servo press that can continuously change these conditions, 10) optimization of lubricant technology, and 11) reduction of work environment load. Here, 1) ~ 4) and 7) can be categorized as goals, 8) and 9) as specific items to be considered for achieving the goals, 5) and 6) as basic technologies that support the research, and 10) and 11) as reduction of environmental load in a wide sense. To put it in other words, the dynamic recrystallization and grain refinement were placed as the base of physical phenomena to achieve the goal, and careful R&D was conducted for the fluctuating factors 8) and 9). I think you can arrange the paper claiming you did your considerations with strong focus on the reduction of the environmental load. Using the above argument as your reference, please take on the challenge to build the logic of the paper in one diagram.

Answer (Naobumi Saito)

Thank you for providing the diagram for the integration of the elemental technologies. The reason "increase in formability of the forging material" was necessary in this R&D was because the forging material was the continuous cast bar with grain diameter of 100 μm or more. In the extruded material that is used conventionally as forging material, efforts to achieve increase in formability is not necessary. Therefore, I added the phrase "development of the forging technology for continuous cast bars," corrected some parts of the diagram that you provided, and created Fig. 12. Other parts were also corrected. Chapter 6 was newly added along with Fig. 12, and the combination of elemental technologies was discussed therein.

3 Relationship with the NEDO Project

Question & Comment (Akira Kageyama)

I think this research is about utilizing the results of the NEDO Project and going on to do the advanced version of R&D. I think it is good to show both the results of the NEDO Project and the joint research, but please describe clearly from where to where is the NEDO Project and from where to where is the joint research. When I read the second draft, it seems that the results of the NEDO Project is to the end of chapter 4. If so, I think you should summarize the results of the NEDO Project at the end of chapter 4 (put the NEDO Project report in your references). Then, the introductory part of chapter 5 can be, for example, as follows: "We held careful discussion on the results of the aforementioned NEDO Project with Miyamotokogyo from the perspective of applying them to actual practice. As a result, we were able to share the recognition that it was important to set the goal of developing the forging technology to obtain high-strength, high-accuracy formed products at temperatures less than 200 °C, and that the grain refinement was necessary to accomplish this. Setting these two as common goals, AIST and Miyamotokogyo conducted the joint research. In the course of discussion, the following points were proposed for the processing cost, environmental measures, and workplace environment, as merits of low-temperature forging."

Answer (Naobumi Saito)

As the reviewer indicated, up to the end of chapter 4 is about the NEDO Project. In the second draft, Reference [1] cited in chapter 2 is the explanation of the essence of the NEDO Project results, but I think it is more appropriate to cite the follow-up evaluation of the NEDO Project (published version). Therefore, the evaluation resources were cited in chapters 2~4, and I corrected the text so it would be clear that these are the NEDO Project results. In the third draft, Reference [1] is the follow-up evaluation of the NEDO Project (published version). For the goal setting of Subchapter 5.1, I followed your indication and corrected the text.

4 Comparison of the forged product

Comment (Akira Kageyama)

In the introduction, you mention that the magnesium alloys are not widely used compared to aluminum alloys. You mention the corrosiveness, plasticity processing, and total cost as reasons. Please consider showing the current situation of the magnesium alloys and the goal of this research, using the aluminum alloy as reference, in the form of a table. In that case, you should break the cost down into, for example, costs of material, manufacturing and processing, energy consumption, or size adjustment. Avoid the expression of high or low, but instead provide something like a cost index. By presenting this, I think the meaning of "promising candidate" that you describe in the abstract can be understood well by the readers who are not specialists of lightweight metal. In the market, people are looking at the total performance compared to aluminum, and if this is shown, the corrosiveness that is the main weakness of magnesium may be offset by its total performance.

Answer (Naobumi Saito)

I had coauthor Sekiguchi of Miyamotokogyo to provide the comparison table for magnesium and aluminum forged products, and added it as Table 1.

5 Table 1

Question & Comment (Akira Kageyama)

Is it correct that Table 1 shows the comparison of the properties between the magnesium and aluminum alloys in the preliminary stage before the start of this research?

1) Please add the density of the two metals (Mg = 1.738, Al = 2.70)

to the table. Since the magnesium alloy contains bits of Al and Zn, the density may be slightly higher than 1.738, but I think this will allow you to show the weight reduction to about two-thirds of the aluminum alloy. Also, for the weight reduction rate 30 % or 20 %, against what are they reduced?

2) I think you should show Table 1 at the end of section 5.2.6 again, and compare the magnesium alloy (conventional), aluminum alloy, and the results/data of this research as Table 3. This is because the superiority of the magnesium alloy against aluminum alloy in terms of weight reduction will be clarified in Table 1, while the comparison of conventional technology and result of this experiment for magnesium alloy will be understood in Table 3. I shall leave it up to the author to include the aluminum alloy in Table 3 again, but the reviewer thinks that you should do so from the following reasons:

- The comparison (competing technology) in the market is against aluminum alloy.
- While the conventional magnesium alloy was unlikely to replace the aluminum alloy in the points of strength, elongation, size accuracy, and cost of finished forged products, the possibility became apparent through this research. Of course, the conventional magnesium alloys used currently can be replaced relatively easily, but that alone will not expand the market for magnesium alloy.

Answer (Naobumi Saito)

As the reviewer indicated, Table 1 is the comparison result of the stage before the start of R&D.

1) I added the specific gravities of pure magnesium and pure aluminum in Table 1. According to co-author Sekiguchi of Miyamotokogyo, the estimate of weight reduction was calculated for small automobile parts including the iron mount for rubber vibration isolator and the structural support materials such as engine mount and link arms. The figures for specific gravity do not entirely contribute to the weight reduction as the weight reduction is slightly lost since the stiffness (elastic coefficient) is insufficient.

2) I added Table 3 as you indicated in section 5.2.6.

6 Processing cost

Question & Comment (Akira Kageyama)

In chapter 5, you refer to the processing cost, environmental measures, and workplace environment. For processing cost, please indicate the following differences: 1) special furnace and infrared heater = consumed electric power, 2) reduction in process, cost of cutting, and 3) mold lifespan. You say that the total of these is 20~30 %, but the reader cannot see which one is the largest contributor. Since the actual numbers may be a corporate secret, you can show them as indexes. Also, what kinds of worsening work environment and environmental load are there in using graphite? You also say “product accuracy increases by low-temperature process.” Is this related to the product of coefficient of thermal expansion and temperature difference?

Answer (Naobumi Saito)

Coauthor Sekiguchi provided us with the particulars of the processing cost, and I added this as Table 2 in the paper. However, he commented that the figures are not that precise. The worsening of the work environment and increased environmental load by graphite were explained in the paper. The reason for the improvement of product accuracy by low-temperature forging is as you indicated.

7 Basic core technology of AIST

Question & Comment (Toshimi Shimizu)

You mention that the structure control, analysis, and evaluation technologies of metal materials are the basic core technologies in which AIST excels. However, I think universities

and other public research institutes have similar and equivalent potential. Can you explain in detail the potential that only AIST has? In relation to this, can you show by figures or tables the latest research trends of forging technology in Japan and overseas, and the relationship to AIST technology? In the first draft, you use a lot of photographs. Although they may be excellent proofs of direct evidence for readers in your field, the general reader cannot understand the difference. Can you show the results and proofs using numerical tables?

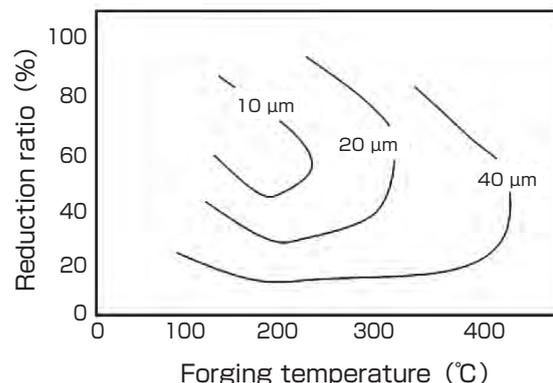
Answer (Naobumi Saito)

The point of this R&D is that the forging of magnesium alloy continuous cast bar that was never used before as forging material was made possible by actively incorporating the phenomenon of dynamic recrystallization, for which academic research has been done extensively, into the manufacturing process. It can be said that AIST bridged the basic academic result and the manufacturing process to enable such technology to be realized, and I think this is AIST’s potential. This is actual practice of the AIST slogan, “Technology to Society,” and I added these points to the conclusion. Concerning the latest research trends of forging in Japan and overseas, I will not add them because this paper centers on the results of joint research with a company, and the content will become too scattered if I discuss the overall forging technology. I added photographs and graphs in appropriate places to enhance the understanding of general readers.

8 Contour map showing the effect of dynamic recrystallization as basic core technology

Question & Comment (Akira Kageyama)

The major point of the technology in this paper is to decrease the grain diameter by one digit through dynamic recrystallization. If temperature and reduction ratio affect the dynamic recrystallization, I think you should consider expressing this phenomenon using a kind of contour map where the grain diameters of the crystals are shown on the X-Y two dimensional coordinates. For example, from the data that the authors have, using the AZ91 alloy or AZX91 + Ca alloy, can you use temperature as the x-axis and reduction ratio as the y-axis to show the obtainable grain size? (The figure shown below is only for reference.)



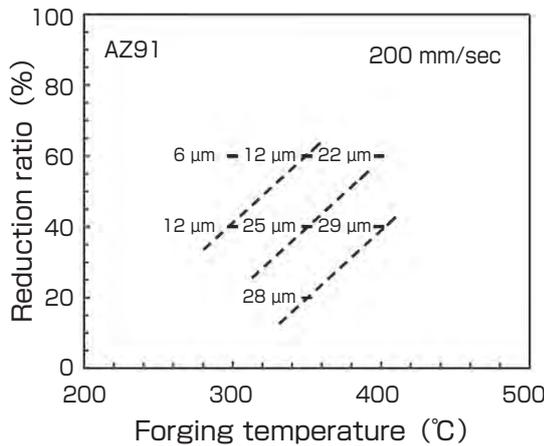
Conceptual diagram of the relationships among forging temperature, reduction ratio, and grain diameter

This data will be the process window itself, and is extremely important in realizing the technology. Also, does the strength of the formed parts increase if the grain diameter decreased from the order of 100 μm to 5~20 μm? If so, please state the mechanism of strength improvement (this can be partially hypothetical). If you continue this discussion, we come to the question that how many μm is the optimal grain diameter. If you discuss this point also, I think it will further help the verification of AIST’s basic

core technology (composition control, analysis, and evaluation technologies).

Answer (Naobumi Saito)

The point you indicated had an important meaning in the R&D for the NEDO Project. Therefore, we attempted creating a figure just like the one you indicated based on the data in Fig. 3, in the discussion of ideation, hypothesis setting, and combination of elemental technologies for the NEDO Project. However, we did not have sufficient quantity of data, and the figure was not very convincing. Therefore, we used Fig. 3 as it is shown in the paper. For reference, I show you the figure that we tried to create.



Reference: Relationship between the forging temperature, reduction ratio, and grain diameter created from the experimental result

The fact that the strength increases at room temperature by

refining the crystal grains of metal materials is already known as the Hall-Petch Relation. We added this in the text of subchapter 3.1.

9 Forged prototype

Question (Toshimi Shimizu)

The company selected the square pin heat sink as the forged prototype, and conducted the low-temperature forging process based on the forging blanks and basic data provided by AIST. In the first draft, only the results where the forging temperature was altered was shown, but didn't you come across other issues that you had to overcome during the prototyping and development? It seems that contrary to the background where "it was difficult to satisfy the mechanical property by the conventional forming process for the magnesium alloy" that you mention in the beginning of the paper, the issues were very easily overcome.

Answer (Naobumi Saito)

During the prototyping and development, we did not hear from the company about any new issues that had to be overcome. Also, the prototype (heat sink) is not an item that requires strength, so we did not conduct the evaluation for mechanical property. However, through the microstructure observation of the pin part of the heat sink, we confirmed that the grains had been refined to 10 μm or less. Therefore, we think it has high strength. The idea of realizing grain refinement by dynamic recrystallization during the forging process was the "Columbus' egg" or seemed difficult but was easy once it had been done. Although it is now taken for granted, we never thought of it when the Project started, and I would like to emphasize that after discussing a lot with the companies and universities, it was proposed by AIST. Also, the magnesium alloy is a material that easily undergoes grain refinement by dynamic recrystallization, and the development of this research whose key point was grain refinement went relatively smoothly as a result.

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
 Revised October 24, 2008
 Revised March 23, 2009
 Revised August 5, 2010
 Revised February 16, 2012
 Revised April 17, 2013
 Revised May 9, 2014
 Revised April 1, 2015

1 Types of articles submitted and their explanations

The articles of *Synthesiology* include the following types:

- Research papers, commentaries, roundtable talks, and readers’ forums

Of these, the submitted manuscripts of research papers and commentaries undergo review processes before publication. The roundtable talks are organized, prepared, and published by the Editorial Board. The readers’ forums carry writings submitted by the readers, and the articles are published after the Editorial Board reviews and approves. All articles must be written so they can be readily understood by the readers from diverse research fields and technological backgrounds. The explanations of the article types are as follows.

① Research papers

A research paper rationally describes the concept and the design of R&D (this is called the scenario), whose objective is to utilize the research results in society, as well as the processes and the research results, based on the author’s experiences and analyses of the R&D that was actually conducted. Although the paper requires the author’s originality for its scenario and the selection and integration of elemental technologies, whether the research result has been (or is being) already implemented in society at that time is not a requirement for the submission. The submitted manuscript is reviewed by several reviewers, and the author completes the final draft based on the discussions with the reviewers. Views may be exchanged between the reviewers and authors through direct contact (including telephone conversations, e-mails, and others), if the Editorial Board considers such exchange necessary.

② Commentaries

Commentaries describe the thoughts, statements, or trends and analyses on how to utilize or spread the results of R&D to society. Although the originality of the statements is not required, the commentaries should not be the same or similar to any articles published in the past. The submitted manuscripts will be reviewed by the Editorial Board. The authors will be contacted if corrections or revisions are necessary, and the authors complete the final draft based on the Board members’ comments.

③ Roundtable talks

Roundtable talks are articles of the discussions or interviews

that are organized by the Editorial Board. The manuscripts are written from the transcripts of statements and discussions of the roundtable participants. Supplementary comments may be added after the roundtable talks, if necessary.

④ Readers’ forums

The readers’ forums include the readers’ comments or thoughts on the articles published in *Synthesiology*, or articles containing information useful to the readers in line with the intent of the journal. The forum articles may be in free format, with 1,200 Japanese characters or less. The Editorial Board will decide whether the articles will be published.

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*, except 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

3.1.1 Articles may be submitted in Japanese or English.

Accepted articles will be published in *Synthesiology* (ISSN 1882-6229) in the language they were submitted. All articles will also be published in *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 within 2 months after the original edition is published.

3.1.2 Research papers should comply with the structure and format stated below, and editorials should also comply with the same structure and format except subtitles and abstracts are unnecessary.

3.1.3 Research papers should only be original papers (new literary work).

3.1.4 Research papers should comply with various guidelines of

research ethics

3.2 Structure

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

3.2.2 Title, abstract, name of author(s), keywords, and institution/contact shall be provided in Japanese and English.

3.2.3 The manuscript shall be prepared using word processors or similar devices, and printed on A4-size portrait (vertical) sheets of paper. The length of the manuscript shall be, about 6 printed pages including figures, tables, and photographs.

3.2.4 Research papers and editorials shall have front covers and the category of the articles (research paper or editorial) shall be stated clearly on the cover sheets.

3.2.5 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.

3.2.6 The abstract should include the thoughts behind the integration of technological elements and the reason for their selection as well as the scenario for utilizing the research results in society.

3.2.7 The abstract should be 300 Japanese characters or less (125 English words). The Japanese abstract may be omitted in the English edition.

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

3.2.9 The article submitted should be accompanied by profiles of all authors, of 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 contributions to the paper are included.

3.2.10 Discussion with reviewers regarding the research paper content shall be done openly with names 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 part of the article.

3.2.11 If there are reprinted figures, graphs or citations from other papers, prior permission for citation must be obtained and should be clearly stated in the paper, and the sources should be listed in the reference list. A copy of the permission should be sent to the Publishing Secretariat. All verbatim quotations should be placed in quotation marks or marked clearly within the paper.

3.3 Format

3.3.1 The headings for chapters should be 1, 2, 3..., for subchapters, 1.1, 1.2, 1.3..., for sections, 1.1.1, 1.1.2, 1.1.3, for subsections, 1.1.1.1, 1.1.1.2, 1.1.1.3.

3.3.2 The chapters, subchapters, and sections should be enumerated. There should be one line space before each paragraph.

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

3.3.4 For figures, image files (resolution 350 dpi or higher) should be submitted. In principle, the final print will be in black and white.

3.3.5 For photographs, image files (resolution 350 dpi or higher) should be submitted. In principle, the final print will be in black and white.

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

Journal – [No.] Author(s): Title of article, *Title of journal* (italic), Volume(Issue), Starting page-Ending page (Year of publication).

Book – [No.] Author(s): *Title of book* (italic), Starting page-Ending page, Publisher, Place of Publication (Year of publication).

Website – [No.] Author(s) name (updating year): Title of a web page, Name of a website (The name of a website is possible to be omitted when it is the same as an author name), URL, Access date.

4 Submission

One printed copy or electronic file (Word file) of manuscript with a checklist attached should be submitted to the following address:

Synthesiology Editorial Board
c/o Public Relations Information Office, Planning Headquarters, National Institute of Advanced Industrial Science and Technology(AIST)
Tsukuba Central 2 , 1-1-1 Umezono, Tsukuba 305-8568
E-mail: synthesiology-ml@aist.go.jp
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 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).

Inquiries:

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Letter from the editor

This is the eighth year since the launch of *Synthesiology*. The “Messages from the Editorial Board,” the purpose of which is to briefly present the objective of this journal, has been renewed and retitled “Aim of *Synthesiology*,” and is now placed at the last page. In the previous “Messages,” it was written that *Synthesiology* was launched to accumulate as knowledge what should be done to make good use of research results in society. This is one of the solutions to the issue raised that the researchers themselves must engage in *Full Research* that actively bridges the large gap between their research activities and social contribution. The “Messages” that was about one page long has been shortened to half a page. I feel the passion of the Editorial Board members who wish to establish the identity of *Synthesiology* in a readily understandable and concise manner, and their thoughts are condensed in the subtitle, “Utilizing the fruits of research for social prosperity.” I think that even such a short explanation may help the readers understand owing to the seven-year history behind the journal. I would like to finish with a closing comment, such as “Looking back over the years, I sincerely feel...,” but I do not feel qualified as it has not been long since I became an editor of *Synthesiology*. On the other

hand, I think that I am perhaps able to see great significance in the change that may seem rather small outwardly in the history of this journal, because my involvement is still short. There may be no need to reaffirm the objective of *Synthesiology* at this point, particularly for the readers who read everything all the way to the “Letter from the editor.” Yet, you may perhaps enjoy tracing the history of attempts to spread *Synthesiology* if you start at “Preface: A journal of original papers of *Type 2 Basic Research*” in the Premier Issue, go through the articles on the roundtable talks that appear occasionally, and then compare the new “Aim” and the old “Messages.”

The simplification of “Messages” in this issue and the addition of “Highlights of the Papers” which started two issues ago are examples of attempts to have more people read this journal and to solicit more submissions from outside AIST. We have made various efforts for the diffusion of the journal, and the Editorial Board is constantly thinking of ways to improve the journal. We shall appreciate it if you could send us your comments on how *Synthesiology* can be diffused further.

(Hiroaki HATORI, Executive Editor)

Aim of Synthesiology — Utilizing the fruits of research for social prosperity —

There is a wide gap between scientific achievement and its utilization by society. The history of modern science is replete with results that have taken life-times to reach fruition. This disparity has been called the *valley of death*, or the *nightmare stage*. Bridging this difference requires scientists and engineers who understand the potential value to society of their achievements. Despite many previous attempts, a systematic dissemination of the links between scientific achievement and social wealth has not yet been realized.

The unique aim of the journal *Synthesiology* is its focus on the utilization of knowledge for the creation of social wealth, as distinct from the accumulated facts on which that wealth is engendered. Each published paper identifies and integrates component technologies that create value to society. The methods employed and the steps taken toward implementation are also presented.

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Highlights of the Papers in *Synthesiology*

Research papers

Proposal for technology architecture analysis

—*Application of an analysis method to the development of car navigation systems*—

T.NOMI and H.IKEDA

Clean and practical oxidation using hydrogen peroxide

—*Development of catalysis and application to fine chemicals*—

Y.KON, S.TANAKA and K.SATO

Development of plastic certified reference materials (CRMs) to cope with restrictions on hazardous substances

—*CRMs for analysis of heavy metals and brominated flame retardants regulated by RoHS directive*—

A.HIOKI, M.OHATA, S.MATSUYAMA and S.KINUGASA

Development of forging process for magnesium alloy continuous cast bars

—*Forging process utilizing grain refinement*—

N.SAITO, H.IWASAKI, M.SAKAMOTO, K.KANBARA and T.SEKIGUCHI

Editorial policy

Instructions for authors

Aim of *Synthesiology*

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