Materials Outlook for Energy and Environment

New Material Science of the 21st Century toward the Solution of Energy and Environment Issues

~For You Looking to Become a Material Scientist~
The problems of global warming and securing energy resources are crucial challenges that the entire world is facing now. Japan has been trying to become a front runner of realizing sustainable societies by advanced science and technology, and has focused on the development of the technologies for utilizing natural energy with higher efficiency and higher functionality, photocatalysts, fuel cells, high efficiency power generation, energy saving lighting, IT products, and other eco-technologies. These technologies are based on the research of new materials.

Fortunately, as Japan has accumulated a wealth of research and development in materials-related fields, it is the key national strategy to create a succession of new materials continually on the fundamentals of research base. In research and development on materials science, an accumulation of results based on a long-term perspective and a stable research environment are necessary. Thus, as a national effort, it is extremely important to gain wide public understanding and achieve steady progress in research.

In this publication, researchers who are directly involved in R&D work outline the current status and future directions of the materials technologies which are related to prevent global warming and secure energy resources from the viewpoint of materials science. We sincerely hope that this will give all readers a better understanding of these issues, and will contribute not only to solving environmental and energy problems in Japan, but also various problems of a global scale.
# Contents

**Preface**

**Chapter 1. Encouraging Material Science**

**Chapter 2. Trends in Materials Research for the Environment and Energy**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Domestic Trends</td>
<td>3</td>
</tr>
<tr>
<td>International Trends</td>
<td>7</td>
</tr>
</tbody>
</table>

**Chapter 3. Electron Energy Materials**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overview</td>
<td>15</td>
</tr>
<tr>
<td>Solar Cell Materials</td>
<td>16</td>
</tr>
<tr>
<td>LED Materials</td>
<td>18</td>
</tr>
<tr>
<td>Materials for Electronic Products</td>
<td>20</td>
</tr>
<tr>
<td>Thermo-Electric Conversion Materials</td>
<td>22</td>
</tr>
</tbody>
</table>

**Chapter 4. Chemical Energy Materials**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overview</td>
<td>25</td>
</tr>
<tr>
<td>Materials for Hydrogen Production and Storage</td>
<td>26</td>
</tr>
<tr>
<td>Photocatalytic Materials</td>
<td>28</td>
</tr>
<tr>
<td>Fuel Cell Materials</td>
<td>30</td>
</tr>
<tr>
<td>Secondary Cell Materials</td>
<td>32</td>
</tr>
<tr>
<td>Corrosion-Resistant Materials</td>
<td>34</td>
</tr>
</tbody>
</table>

**Chapter 5. Materials for High-Efficiency Major Power Plants**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overview</td>
<td>37</td>
</tr>
<tr>
<td>High Temperature Materials for Gas Turbine Power Generation</td>
<td>38</td>
</tr>
<tr>
<td>Ultra Supercritical Coal-Fired Power Generation Materials</td>
<td>40</td>
</tr>
<tr>
<td>Fusion/Fission Power Generation Materials</td>
<td>42</td>
</tr>
</tbody>
</table>

**Chapter 6. Materials for Energy Transmission and Conversion**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overview</td>
<td>45</td>
</tr>
<tr>
<td>Superconducting Materials</td>
<td>46</td>
</tr>
<tr>
<td>Magnetic Refrigerants</td>
<td>48</td>
</tr>
<tr>
<td>Permanent Magnetic Materials</td>
<td>50</td>
</tr>
<tr>
<td>Mechanical Response Materials</td>
<td>52</td>
</tr>
</tbody>
</table>
6.6 Low-Friction Materials
6.7 Light Structural Materials
6.8 High Temperature Materials for Aeroengines

7. Nano-driven Energy/Environmental Materials

7.1 Overview
7.2 Atomic Switch Materials
7.3 Nanoscale Materials
7.4 Nanoassembly Materials
7.5 Nanostructure Control Materials

8. Clean Processing and Materials for That

8.1 Overview
8.2 Adsorbent Materials
8.3 Separation Membrane Materials
8.4 Exhaust Gas Catalyst Materials
8.5 Nature Tech Materials

9. Diagnosis and Lifetime Prediction Technologies

9.1 Overview
9.2 Crack Growth and Life Assessment Techniques
9.3 Assessment of Fatigue and Life Assessment Techniques
9.4 Assessment of Creep and Life Prediction Techniques
9.5 The Assessment of Corrosion, Stress Corrosion Cracking (SCC) and Lifetime Assessment Techniques
9.6 Methods to Evaluate Degradation and Damage
Chapter 1. Encouraging Material Science

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1. Environmental and energy issues

2007 was an important year in the struggle against global warming. As you all know, the IPCC and former American Vice President Al Gore were awarded the Nobel Peace Prize. This was the moment when people recognized that greenhouse gases are major contributors to global warming and that the global warming issue can no longer be ignored. At COP13 held on the island of Bali in Indonesia, a roadmap was unveiled for the reduction of greenhouse gases following the Kyoto Protocol, and an international framework with the participation of the major greenhouse gas-emitting nations was finally drawn up. One could say that 2007 was the year that people around the world could clearly see the starting line in the race against global warming.

The Kyoto Protocol came into effect in April 2008. Japan’s reduction target over five years is to reduce greenhouse gas emission levels to 6% below what they were in 1990. However Japan has increased them by more than 8% since 1990. In line with international treaties that call for a 50% reduction by 2050, people are demanding that drastic measures be taken.

Carbon dioxide accounts for about 90% of Japan’s greenhouse gas emissions. Most of this comes from the combustion of petroleum, coal, natural gas and other fossil fuels. To reduce emissions of greenhouse gases, we need to develop technologies that allow us to use energy efficiently and we need to switch over to using renewable sources of energy.

Although environmental issues and energy issues appear to be two separate problems, it all depends on whether we look at human economic activity as an input or as an output. The energy problem is clearly an input, and environmental problem is clearly an output. In creating a sustainable society, the truth of the matter is that we have to reduce the inputs and make them renewable, and we have to use the inputs in our economic activities more efficiently, and reduce outputs and make them safe.

2. Japanese civilization

The opening sentence of Yukichi Fukuzawa’s *Gakumon no Susume* (Encouraging Learning, published in 1882) reads, “It is said that heaven creates no man above other men and creates no man below other men.”

The historian Samuel P. Huntington divided up the world into eight civilizations (Western European, Confucian, Japanese, Islamic, Hindu, Slavic, Latin American and African), counting Japanese civilization as one of the eight great civilizations of the world. The historian Arnold J. Toynbee reaches the same conclusion, writing that in Asia, Japan has been the only country to succeed in rapid modernization and become a nation of affluence, and that Japanese civilization is different to Confucian (Chinese) civilization.

Through *Gakumon no Susume*, the great Fukuzawa spoke of the importance of practical science. Fukuzawa reasoned that while heaven might create all men the same, the fact that some were above others was the result of learning. He worked to quickly introduce practical science (learning) to replace traditional Japanese literature which until that time had been based on Confucianism and the Chinese classics. Science would clearly show the principles and fundamentals of natural phenomena and enable them to be put to practical use. One can say that Japan’s modernization follows this extending line, and as a result, Japanese civilization achieved enlightenment.

3. The fundamentals of traditional ways of thinking

Before looking at the status of material science in Japanese civilization, I will introduce the traditional Japanese way of thinking.

According to Takeshi Umehara, religion is the foundation of all civilizations. Western Civilization is founded on monotheistic Christianity. In the Middle East it is Islam. Huntington’s grouping of the world’s civilizations can also be based on religion. Since the Meiji Period in Japan, on what religion has Japanese Civilization been based?

Shichiihei Yamamoto makes a clear analysis that it is the religious-like belief of the Japanese that the framework of society is static and unlikely to change over time. Yamamoto points out that this belief originated in the Edo Period, which clung to an immovable social system for 250 years based on a policy of international isolation. This social system, that included a rigid class system under which children of farmers would be destined to be farmers, where foreign trade was prohibited, and where Christianity — which believed in the absoluteness of God — was suppressed, was a means to create a sense of value based on an unchangeable societal structure and to stabilize political power.

The Japanese have traditionally viewed nature as something that does not change over time. Unlike Westerners, Japanese rather like the expression of “letting nature take its course.” They probably feel that this is the natural way things should be. In the Edo Period, people’s sense of value changed, from those based on nature to those based on society.
The basis for this traditional way of thinking played a tremendous role in the introduction of practical science to Japan from the Meiji Period onwards. Practical science was very convenient as a means to make the framework of society even more solid and immobile. The construction of the railways, road network and other social infrastructure and the development of core industries, it is not too much to say that the Japanese traditional ways of thinking built Japanese Civilization. You can sense Fukuzawa’s clever strategy in the background.

4. Material science up until the present

Material science is also a practical science. Unlike culture, the purpose of practical science is to be put to real use. Material science has been used as a means to immobilize the framework of society based on the traditional ways of thinking. In Europe, material science is a little different and has a strong sense of being used to get a better understanding of the principles of natural phenomena. In my area of specialty, which is thermoelectric materials, a professor of Cardiff University received a knighthood from the Royal Household last year in recognition of many years of contributions to science.

In Japan, material science has effectively developed convenient materials desired by society in response to social needs. Material science has played a major role in supplying steel, cement, plastics, semiconductors and other materials that society needs.

5. Material science today

In 1989 the Berlin Wall came tumbling down. Japan said goodbye to the Showa Era and ushered in the Heisei Era with the ascension of the new Emperor to the throne. You are all no doubt aware of the tremendous changes to World Order that occurred from about that time onwards. Japan lost sight of its goal of creating a place for itself in the world and a sense of stagnation descended upon Japanese society.

Material science as a means sensed this feeling of stagnation and had no choice but to search for a new direction for research and development. In 1996 the First Phase of the Science and Technology Basic Plan was formulated to show material science the path that the Japanese government should pursue. At present the Science and Technology Basic Plan has entered its third phase.

Today, more so than in the past, I feel that material science is rushing along the practical science road, not to make the framework of society more rigid, but to appeal their existence to each other in the fractionated various material fields. At the moment a lot of attention is begin given to material technology that looks like it will soon be useful, and material science fields that have high productivity. The fact of the matter is that we are pushing ahead with research and development that is narrow, deep, separate and short-term.

6. Encouraging new material science

It has been pointed out that if the current environmental and energy problems continue as at present, we will find ourselves in a very difficult situation by the middle of this century. The same situation applies to our mineral resources. Once we become aware that environmental and energy problems are a real part of the growth of material science, then we need to revise the approaches to practical science. We need to return to basics: the pursuit of the principles of natural phenomena, and build a new kind of material science that is not captive to specific fields of materials or practical science.

This is where the mission of NIMS lies: to face down these tough environmental and energy problems, and rebuild material science in an inter-connected manner and discover solutions to problems.

In Japan, we have a view of nature as being an “unchangeable system” and the traditional way of thinking that is based on this view. This approach forms the cornerstone of Japanese Civilization. In recent years we have seen with our own eyes the unusual weather and felt the warming that has occurred. All around the world there are many people who are worried about environmental and energy problems including the unstableness of the Earth itself. The Earth is questioning our view of nature and our traditional ways of thinking.

The time has come to focus the wisdom of Japanese Civilization. To all of you out there who are involved with materials research: liberate material science from the shackles of practical application and tell the rest of the world about new material science by integrating wide range of sciences based on our accumulated materials research activities and by pursuing principles of phenomena! Let’s confront environmental and energy problems and together aim to create a sustainable society.

In this paper, we set up “key items” and/or “keywords” of material science for each type of material in each chapter. Based on this, we have attempted to introduce each material. I would this to be the first step towards a new material science.
Chapter 2. Trends in Materials Research for the Environment and Energy

2.1 Domestic Trends

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1. Principles and goals of the 3rd Phase of the Science and Technology Basic Plan

The 3rd Phase of the Science and Technology Basic Plan, approved by the Cabinet on 28 March 2006 can be summed up as having “3 principles, 6 major goals and 12 medium goals.” Within Principle 2 of the Plan “Creating a Source of National Resources — Working to Create a Nation that is Internationally Competitive and Capable of Sustainable Development,” there are two major goals (3 and 4). Within Major Goal 3, a high priority has been placed on “The Coexistence of the Environment and the Economy — Achieving Sustainable Development in which both the Environment and the Economy can be Managed.” Major Goal 3 has two more tangible medium goals: Medium Goal 4 “Overcoming global warming and energy issues” and Medium Goal 5 “Achieving a recycling society that is in harmony with the environment.” As can be seen, energy and the environment are both very important areas for national policy-making. I will start by introducing the important research and development themes listed in the Promotion Strategies for the Various Fields of Science — Contributing to the World, Society and the Nation Through Science and Technology — in the 3rd Phase of the of the Science and Technology Basic Plan produced by the General Council on Science and Technology.

Nano/materials field, one of the four important fields, has a special role to play as the basis in a wide range of research, and important research and development themes in relation to the environment and energy are defined as below.

Firstly, in the field of materials:
[Overcoming the energy problem]
- Material technology to enable the practical use of energy that is still not widely used
- Innovative material technology for highly efficient energy use

[Creating a recycling society in harmony with the environment]
- Material technology to help in measures against toxic substances and materials
- Technology for the substitution and effective use of scarce resources
- Material technology to improve and protect the environment
Also, the field of nano-electronics:
- Energy saving and environmentally friendly nano-electronics that make the environment and the economy compatible with one another

These research themes in the field of nano/materials will yield results in the areas of the environment and energy and will uncover interrelated, important things related to these areas.

Let’s outline the kinds of goals that were set in the environmental and energy fields.

We can come up with a large number of detailed objectives in the environmental field, and to save space, we will leave the details to the literature and introduce as simple a list as possible.

♦ The environmental field
The topics below marked by large bullet points have been selected as strategically important sciences and technologies.

[Climate change research]
- Climate change: make observations in different parts of the world, and develop ways to accurately forecast climate change and assess its effects.
  - Via satellite, observe greenhouse gases and the environment of the upper layer of the Earth’s surface
  - Forecast climate change in the 21st Century using climate models
  - Predict and manage climate change risk and formulate plans to encourage social behaviour that does not contribute to global warming
- Technology for countermeasures: to reduce greenhouse gas emissions, atmospheric pollution and marine pollution. These measures will target methane, di-nitrogen monoxide, halogenated greenhouse gases, etc.

[Chemical substance risk and safety management research]
- Enabling the risk and safety management of chemical substances to contribute to a virtuous-circle relationship between the environment and the economy.
  - Forward-looking risk assessment and management for new substances and materials
  - Risk management and assessment that is compliant with the framework of international cooperation
  - Humanities and social science related to risk management

[Water/substance circulation and water catchments]
- Enabling healthy water cycles and sustainable water use.
  - The observation of water catchments on a global and regional scale, and key environmental information
  - Planning scenarios for realizing water catchment areas and urban areas that can coexist with the natural environment

[Ecological management research]
- The protection and utilization of sustainable ecologies.
  - The observation, analysis and assessment of biological
Chapter 2

[The diversification of energy sources]

• Ecological service management technology for wide-area combined ecosystems

[3R technical research]
- Enabling the effective use of resources and the reduction of waste through the 3Rs (Reduction, Reuse and Recycling) and the technology to enable the substitution of scarce resources.
- Technology for system analysis, assessment and planning, to help put the 3Rs into practise
- Technology for the utilization of useful substances and the management of harmful substances that is compatible with international 3R

[Research into biomass use]
- Utilizing biomass technology developed in Japan to effectively use biological resources.
  • Technology to utilize plant-based biomass energy
  • Technology for systems using local sustainable biomass

We can see from the above that the atmosphere, fresh water, seawater, soil, biomass, chemical substance management and technologies relating to the 3Rs are all important key words.

Next is the energy field, where there is the sense of bringing innovation to the technology that is currently used to supply energy, as well as developing new energy sources.

♦ The energy field

[The diversification of energy sources]

a. Promoting the use of nuclear power
   - The focus is on such areas as ensuring safety and recycling nuclear fuel to help position nuclear power as a stable supply of energy and a key source of power to combat global warming.
   — Technologies for the next generation of light-water reactors and the advanced use of light-water reactors, fast-breeder reactor cycles, uranium concentration and new fuels, reprocessing of spent fuel (light-water reactor fuel), disposal of highly radioactive waste in subterranean layers, measures for the decommissioning and disposal of nuclear facilities and the treatment and disposal of radioactive waste, nuclear fusion energy, fundamental and basic research into nuclear power, research and development of nuclear non-proliferation technologies, high-temperature gas reactors and other innovative nuclear power system technologies.

b. Ensuring the safety of nuclear power
   - The research and development of specifications and safety standards and other measures that are needed in safety inspections is being promoted.

c. Promoting the use of renewable energy
   - The focus is on cost reductions.
   — Technology for the use of solar energy, biomass, waste use, wind power and other renewable energies

d. Hydrogen/fuel cells
   - Expectations are turning towards fuel cell systems and technology for the production, storage and transportation of hydrogen.

e. Promoting the development and use of fossil fuels
   - The focus is on ensuring a steady supply of fossil fuel, and reducing the environmental impact of fossil fuels — particular-ly coal.
   — Technologies for energy resource exploration, fossil fuel mining, petroleum refining and use, clean coal use, new fossil-fuel-based liquid fuel production, highly efficient natural-gas-fuelled power generation, highly efficient gas engine technology, and technology for the recovery and storage of carbon dioxide

[Making energy supply systems more advanced and reliable]
- The idea of the coexistence of large-scale integrated systems and distributed systems has been proposed.
- Electricity supply systems (technologies for power transmission and power system control)
- Electricity storage systems
- Gas supply systems
- Basic technology for the supply of petroleum

[The promotion of measures for saving energy]

a. Measures for the private sector (household and commercial)
   - It is hoped that the growing private sector can make further cuts to their level of energy consumption.
   — Technologies to help homes and buildings use less energy, technologies for highly efficient air conditioning/heating/lighting, highly efficient domestic networked appliances and communication devices, urban systems

b. Measures for the transportation sector
   - Transportation sector accounts for 40% of petroleum consumption. Measures to greatly reduce the levels of energy consumed by private vehicles, whose petroleum consumption has been increased, are expected.
   — Technologies for the next generation automobiles, technologies to make aircraft and ships more energy efficient, and increase the efficiency of physical distribution

c. Measures for industry
   - Promote measures to reduce increasing energy consumption in industries in national level.
   — Processing technology for the manufacture of materials that conserve energy, energy efficient assembly and processing, cooperative systems among industries for the more efficient use of energy

d. Measures linking different sectors
   - Research in topics that are common to all sectors are listed.
   — Technology for the effective use of heat, high-performance devices

These are all important issues that have to be overcome. Research fields have been defined and realistic targets have been created with the hope of achieving tangible results.

The 3rd Phase of the Science and Technology Basic Plan is playing a role in overseeing Japan’s overall research and development activities.

2. “Cool Earth 50”: Technical issues in the government’s measures to combat global warming

The technologies listed below are examples of those that will be needed to achieve the long-term goal to “reduce the level of
global emissions to a half of what they are today by the year 2050" announced by (then) Prime Minister Abe in May 2007. Here we can see an overall view of the technologies that industry hopes will lead to the achievement of this goal.

- Innovative zero-emission coal-fired power generation
  The combination of more efficient coal gasification-fuelled thermal power generation with the means to recover and store carbon dioxide will enable the reduction of emissions from coal-fired power stations, which currently account for 30% of global emissions, to be reduced to zero.
- Advanced nuclear power generation
  The next generation light-water reactors, small- and medium-sized reactors, high-temperature gas reactors, and the development of practical fast-breeder reactors will enable zero-emission nuclear power generation to increase considerably.
- Innovative, efficient and inexpensive technology for the use of solar energy
  Significantly increased conversion efficiency of solar power generation will achieve the economical efficiency on a par with those of thermal power generation, with an interdependent increase in the capacity of storage batteries with reduced costs.
- New technology for the use of hydrogen as an energy source
  Reducing the costs and raising the efficiency of fuel cells will allow fuel cell cars to become much more widely used. This will enable the reduction of emissions from automobiles, which currently account for 20% of global emissions, to be reduced to zero.
- Technology for ultra-high-efficiency low-energy use
  Steel-making in which some of the coke is replaced by hydrogen as the reducing agent will enable a considerable reduction in the greenhouse gas emissions of the steel-making process. This is one example of technology that will make manufacturing processes and machinery far more energy efficient so that they will consume far less energy and generate lower levels of carbon dioxide emissions.

These are some examples of the technologies that will help achieve this emission reduction goal, and are consistent with the 3rd Phase of the Basic Plan.

3. Research and development of materials in the fields of the environment and energy by public research institutions and other bodies

In January 2008, NIMS held a hearing attended by representatives of the following public research institutions and other bodies to learn of their expectations towards and requirements for materials. These institutions and bodies were (in no particular order): The Port and Airport Research Institute, the National Maritime Research Institute, the National Traffic Safety and Environment Laboratory, the Energy Conservation Center, the Central Research Institute of Electric Power Industry, the Japan Environmental Management Association for Industry, the Center for Environmental Information Science, the Railway Technical Research Institute, the Japan Aerospace Exploration Agency, the Japan Atomic Energy Agency, the National Institute for Environmental Studies, the National Institute of Advanced Industrial Science and Technology, and the Public Works Research Institute.

The hopes and expectations raised at the hearing can be grouped in a variety of ways, but we have done roughly according to common material characteristics.

- Environmental impact and low cost: better recyclability, low environmental impact, the collection and supply of material-related data to enable the quantitative assessment of environmental impacts, ensuring the traceability of substance and material data, a reduction in hazardous substances, low prices, availability
- High efficiency: Strength/toughness, strength/brittleness, weight reduction, coefficient of friction, lubricating qualities, abrasion resistance, greater efficiency in separation and concentration/recovery, workability and ability to be processed
- High temperature applications: coefficient of thermal expansion, heat resistance, fire and fuel resistance, thermo-cycle resistance, thermal degradation resistance
- Long life and reliability: corrosion resistance, weather resistance, anti-rusting qualities, saltwater resistance, steel reinforcing rod ant corrosive qualities, corrosive-resistant materials used as paint substitutes, general painted film performance, long-term durability (alkali-silica reaction, salt damage, cracking), fatigue strength, estimation of fatigue strength life and non-destructive testing, weldability, shock resistance, ability to be inspected and repaired, irradiation embrittlement, radiation resistance
- Functionality: catalytic activity, catalytic acid resistance, solar-cell characteristics, battery characteristics, smaller and more efficient fuel cells, higher performance of secondary batteries (energy density, power output, storage capacity), heat recovery performance, thermal conductivity

As we can see, the demands of public and other research institutions vary widely, but there are a large number of issues relating to both the performance of materials and the guarantee of that performance.

4. Related research topics at NIMS

At NIMS, we consider national problems and a wide range of social needs –like the ones above. We identify those problems where we can make use of our research potential and make a contribution, and promote the following five projects as materials research themes in the fields of environment and energy, based on our medium-term plan.

High-temperature materials project
Based on many years of world-class achievement with nickel-based super-alloys and other ultra-high-temperature materials, we carry out basic research to make materials that have higher working temperatures and performance stability. Since our studies are carried out jointly with the private sector, we aim to achieve dramatic improvements in thermal efficiency and move on to practical application within our medium-term plan.

Fuel cell materials project
In this project we tackle new challenges. We are making more
detailed and systematic investigations of the mutual interactive effects of hydrogen and materials to see if they offer potential for use with hydrogen or in fuel cells. For example, researchers at NIMS have discovered a nano-structure-controlled ceria oxide compound that possessed high ion conductivity at a 500 °C or less, compared with zirconia-based compounds that require a temperature of 1,000 °C. We are working to deepen this kind of basic research and are aiming to develop materials that will have the performance allowing them to be put to practical use.

**Superconducting materials project**

In this project, NIMS leads the world in its unique position of carrying out research that ranges from searching for new materials to developing wire technology (1-km class). In recent years, there have been amazing advancements in peripheral technologies such as refrigeration. We are working to raise the working temperature of superconductors from that of liquid helium (4K) to that of liquid hydrogen (20K) and are making progress with individual issues.

**Photocatalytic materials project**

The well-known photocatalyst titanium dioxide has the limitation of only working under ultraviolet light, yet NIMS researchers have discovered several photocatalytic materials that function in the visible light range as well. NIMS is aiming to develop these materials for use in the home environment where they will be able to decompose harmful substances and render them harmless under natural or fluorescent light. NIMS scientists are working to extend the range of wavelengths under which these photocatalysts operate to include visible light, and enhance their decomposing ability and stability.

**High-performance metallic materials project**

In this project, researchers are attempting to respond to conflicting demands by studying steel, magnesium, titanium, aluminium and other metals in a comprehensive manner, based on the results achieved in research into ultra-steel. For example, automobile makers demand both light weight and impact stability. NIMS researchers are studying ways to control the structure of metals that have high strength and are easy to process.

Unfortunately, these five projects alone are not enough to meet society’s wide-ranging and serious expectations. NIMS will strive to carry out even more research and development in the environment and energy field, and is conducting studies and preparation to increase its level of activity.

Fig. 2.1.1 shows NIMS’ basic strategy. NIMS uses nanotechnology and takes the responsibility to conduct research under various themes, such as environmental clean-ups, saving resources, saving energy. NIMS is working hard to create highly functional substances and materials out of ordinary, harmless elements, and to develop material technologies that will allow us to use the energy sources around us, such as sunlight and hydrogen, as much as possible.

There is a tendency, when solving the urgent problems that are right under one’s nose, to set objectively passive technical research goals. While these passive goals may be highly significant and important, NIMS, as an organization engaged in the fundamental research of substances and materials, is seeking to actively change the environment, as shown in Fig. 2.1.2, and is aiming to put forward completely new ideas that can create new resources and energies. For example, those using its research achievements are distributed electrical energy storage, low-loss electricity transmission systems, high-temperature materials for highly efficient power generation, light and high-strength thin-sheet metals, super-long-life non-corroding materials, highly efficient light energy utilization, materials that can recognize and select certain molecules (surfaces, thin permeable films, structures, etc.), and more effective chemical reaction catalysts. NIMS is also looking forward to entirely new recycling technologies of the future, such as ones that will use water, soil, etc. as materials, and those that will utilize the carbon dioxide recycle.

**References**


2) “Invitation to Cool Earth 50,” Ministry of Foreign Affairs, 2007

2.2 International Trends

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1. International Backdrop to Environmental and Energy Research

1.1 Environment and Energy Issues Common to All Mankind

As for international movements over the global warming and energy problems, it has been brought together in details in a wide range of documents, such as the websites of the Ministry of the Environment (1), and the Agency for Natural Resources and Energy’s white paper (2) and NEDO overseas reports (3). To give an overview of the relationship of these two issues with materials science, this article will present an outline of international trends in this section and in Section 1.2, and will introduce some recent trends in the United States, the nation that has the closest relationship with Japan, in Section 1.3, where the directionality of research and development will be discussed.

Global issues are the declining birth rate and growing population of elderly people in the developed countries, the explosive population increase in the developing countries, the food problems, the energy and resource problems and the intensifying worldwide competition in economics and technology. Never before in history has the issue of whether or not the mankind can accomplish sustainable development been taken so seriously.

It is common for many countries including our country to try to find means of escape to development and innovation of the science and technology, to solve the difficult issues of how to develop sustainable energy sources and how to overcome climate change and water shortages (4-7). It is also a common view that the science and technology is the key so as not to leave the unfavourable legacy of past deeds as environmental pollution, resource depletion and other issues, on to the next generation. The scientists have been participating up to now in political initiatives through the places of international politics and have promoted the study of these issues, since it is not possible to solve them by only one country.

Beginning in 1985 with the United Nations Environment Program’s (UNEP) Villach conference on global warming, policymakers and scientists have met and discussed these matters. At the United Nations Conference on Environment and Development held in 1992, the United Nations Framework Convention on Climate Change (UNFCCC) was opened for signature and the majority of the world’s countries signed the UNFCCC with the objective of reducing atmospheric concentrations of greenhouse gases. Ever since the Summit on Sustainable Development (Johannesburg) in 2002, the issue of sustainable development has been a primary subject at G8 summits and the policy proposals have been presented. The Earth Observation Summits, COPs, or signatories’ legislatures, have put forward concrete action plans to achieve the sustainable society. To be noted, the Kyoto Protocol (1997) came into effect in February 2005, and from 2008 to 2012 Japan must reduce its greenhouse gas emissions by 6% compared with the standard year (8). The situation is now critical.

In addition to these international politics, in which individual governments and the environmental scientists have taken part, the material scientists themselves have been lively discussing over the environment and energy from global aspects. For example, at the International Symposium on Sustainable Energy and Materials (ISSEM2007) held in Okinawa in October 2007, scientists discussed the contribution of materials science to sustainable society, eco-materials and elemental strategies. In the energy forum of the MRS2008 Spring Meeting (San Francisco), the discussion included the contribution of materials science, biofuels, catalysts and solar energy. At the NIMS-organized Third World Material Research Institute Forum (WMRIF-3), to be held in 2009, discussion will have a global perspective and will focus on sustainable energy and materials.

1.2 Approaches in Countries on Environmental and Energy Issues

While global energy demand has continued to grow (with China and India at the fore), the OPEC has reduced petroleum production since 1999, causing the petroleum price to rise. Moreover, a hurricane in autumn 2005 which knocked back U.S. petroleum refining output, the Russian economic strategy behind the petroleum supply, and more recently, the speculative surge in oil prices affected by the sub-prime loan crisis, have driven the oil price to high levels.

Against the background of the oil market where there are many uncertainties, the U.S. announced its National Energy Policy (10) in 2001, indicating a shift away from a market-led energy policy, towards the one which emphasizes the energy security. This new energy policy called for measures to strengthen the domestic energy supply, and the international initiatives to protect the environment and to promote developments for the stable supply of energy. The Energy Policy Act (11) in 2005 contained concrete measures for the promotion of energy conservation, renewable energy, resource studies, support for the construction of new nuclear power plants, hydrogen infrastructures, fuel-cell cars and the expansion of the use of bio-fuels. In particular, the U.S. government’s policy of encouraging nuclear power generation will help ensure a greater diversity of energy sources apart from petroleum, and will contribute to the stability of the energy supply. Permits for the construction of new nuclear power plants have been granted in rapid succession, and the nuclear power sector is becoming reinvigorated. In his State of the Union message to Congress in 2006, the President advocated the Advanced Energy Initiative (12) rolling out a new policy of putting the energy security at the forefront.
U.S. policy has made ensuring the energy security an issue of national security; this is different from the political approach taken in Japan. Japan has continued to place “the environment” into the four prioritized areas for promotion (life science, telecommunication, the environment, and nanotechnology & materials) from the 2nd phase of the Science and Technology Basic Plan (2001-2005) and has included “energy” in the other key areas of the second priority. The U.S., on the other hand, mostly regards “the environment” as a part of “energy”. As mentioned earlier, environmental and energy problems are common to all the mankind, and in these recent situations of scarcity, it is inevitable that our nation Japan that has limited natural resources will once again have to do an about-face in its policies concerning the importance of energy.

In the European Union as well, the member countries are revising their energy policies. In autumn 2000, the EC announced its Green Paper on the guarantee of energy security (Towards a European Strategy for the Security of Energy Supply)\(^{14}\), putting forward an energy policy with two main components: 1) reduction in energy demand by promoting the energy conservation and the introduction of renewable energy; and 2) countermeasures to global warming. A European Union’s law officially announced in 2001 calls for 22% of total energy consumption to be supplied by renewable energy sources and 5.75% of all fuel consumption to be bio-fuel by the year 2010. In 2005, an EU Green Paper on increasing the efficiency of energy use called for energy consumption to be reduced by 20% by 2020 through technology for energy conservation. The EU is thus promoting the drastic policies. The EU countries are taking another look at the nuclear power development. Beginning in around 2005, the UK, the Netherlands, Finland and other countries have started to look at the nuclear power generation in a positive light.

Russia is promoting policies to increase energy production. In May 2003, the Russian Cabinet approved the “Russian Energy Strategy to 2030” and appears to be using its petroleum management strategy as a lever for the economic growth. This could raise concern over the EU energy security.

The pattern of global energy consumption is now changing. The major consumers of energy are changing, from the advanced industrialized countries to the economically rapidly growing BRICs countries. Although both China’s and India’s national policies take energy conservation and environmental impact reduction into consideration, they are taking a path to greater energy use with an emphasis on economic growth. Until now, the developed countries have emitted most of the world’s greenhouse gases. However, in future, countries that are not bound by international obligations to reduce emissions of greenhouse gases will increase their levels of energy consumption and it will not be possible to reduce the destruction of the global environment. There are concerns that fossil fuels are growing scarce at an increasing rate.

Together with the environment and energy being of common concern to the mankind, there are also the so-called “North-South” problems of the disparity between the relatively wealthier countries and the relatively poorer ones. For these reasons, it is recognised that cooperation with the developing countries and promoting the efficient use of energy and the guarantee of reliable energy sources are important issues on a global scale\(^{15}\).

Next, the latest trends in U.S. research and development will be described, and their relationships with the fields of the environment and energy, and especially with materials science and technology will be discussed.

### 2. Recent Trends in U.S. Research and Development

#### 2.1 Energy Initiatives in the U.S.

The latest initiative to set the direction of research and development in the United States is the American Competitiveness Initiative (ACI)\(^{16}\) announced in February 2006. The ACI, which spells out ways to “overhaul the systems of the entire country, with “innovation” being the key word,” names three bodies to be the institutions responsible for research and development: the Department of Energy (DOE), the National Science Foundation (NSF) and the National Institute for Standards and Technology (NIST). The ACI budget is apportioned by priority to the three institutions. The important components in the ACI are:

1. Establishment of a position of world leadership through the innovations. Funding for the natural sciences and technologies to be increased to achieve this goal;
2. Promotion of ACI-related research, particularly by the NSF, DOE and NIST (appointed as ACI institutions). Research budgets will be doubled over a 10-year period. Facilities and other infrastructures for users will be significantly enhanced;
3. Leading the world in developing human resources who have talent and creativity; and
4. Promotion of education. The DOE and other national research institutions participate in educational programs.

The ACI clarifies the U.S. policy of taking a position of world leadership using science and technology as the key. As a background to these moves, there are growing concerns that the U.S. is gradually losing its international competitiveness, particularly in the industrial fields. As already mentioned, fears that the U.S. may lose its dominance of the global energy market have become apparent. Fig. 2.2.1 shows the planned budget increases of the ACI-designated research institutions (NSF, DOE and NIST), doubling over a 10-year period. The policy that sought this budget increase is actually conducted in the budget apportionment (to be discussed below).

Together with the ACI, the Advanced Energy Initiative\(^{17}\) put out by the National Economic Council in response to the 2001 National Energy Policy (NEP)\(^{11}\) and the Energy Policy Act\(^{12}\) of 2005 is an action plan of realistic proposals that has the following principle items:

1. Diversifications and security of automobile fuel (hybrid vehicles, bio-fuelled vehicles, hydrogen fuel-cell-powered vehicles);
2. Diversification and security of energy for the home and workplace (coal, nuclear power, solar cells); and
3. Security of existing energy sources and development of new
Chapter 2. Trends in Materials Research for the Environment and Energy

The Advanced Energy Initiative is an attempt to ensure the global initiative concerning the energy...

In response to these moves, the DOE — whose mission is energy research and development — enacted the Office of Science’s Strategic Plan in February 2004, and the DOE Five-Year Plan FY2007-2011 in October 2006. By showing more definite research and development plans, the national research institutions were able to make a positive start, and this is responsible for the recent trends towards the emphasis on energy research and development.

2.2 Trends in Environment and Energy Budgets

In the 2009 budget proposal submitted in February 2008, the budgets for the three national science bodies named by the American Competitiveness Initiative (ACI) as well as the budget for the development of manned space vehicles continue to significantly increase. The budget for national defence research continues to increase, and the amount to be spent on basic defence research in natural science is rising, while the rest of the domestic budgets are, for the most part, flat. Although research investment tends to generally increase, the National Institutes of Health (NIH) biomedical research budget is stagnating; moreover, the budgets for the research and development departments relevant to environment and agriculture have significantly declined.

Concerning “the environment,” the budgets related to the Environmental Protection Agency (EPA) have rather declined, though the research and development within the DOE and specific budgets for research of climate change have increased. Despite the overall shrinking budgets, the federal government investment in research and development increased by 3.5% (4.9 billion dollars) to 147.4 billion dollars, mainly to boost spending on “developmental budgets.” A breakdown of this increase reveals a 6.0% (4.8 billion dollars) increase for DOD weapons and NASA spacecraft development to 85.4 billion dollars in total. The budget for research facilities such as NASA’s international space station and the International Thermonuclear Experimental Reactor (ITER) increase by 6.2% to 4.7 billion dollars.

The budgets of the three ACI institutions (NSF, NIST and DOE’s Office of Science) increase by 15% to 12.2 billion dollars. This large increase has come at the expense of the research funding (mainly Congressional funding) of other government institutions. The overall federal budget for fundamental and applied research will decrease by 0.3% in 2009 to 57.3 billion dollars.

Fig. 2.2.2 shows the general trends in research and development budgets. The total budget for research and development has declined for five consecutive years since peaking in 2004, and has fallen 9.1% compared to that time. It is regarded that selection and concentration have occurred.

Looking at each departmental budget for FY2009 in comparison with FY2008 reveals that the budget for the NSF has increased by 15.5% to 5.2 billion dollars, that of the DOE’s Office of Science by 21% to 4.3 billion dollars — of which the

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<th>Units</th>
<th>FY2006 budget</th>
<th>ACI research FY2007</th>
<th>ACI research FY2016</th>
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<td>$4.10</td>
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<td>Total</td>
<td>$9.75</td>
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Fig. 2.2.1 Planned doubling of budgets to ACI-designated research institutions over a 10-year period.

Fig. 2.2.2 Trends in Research & Development Budgets by Agency, FY1976-2009.
budget for basic energy science (BES) will increase 24% to 1.6 billion dollars. The budget for the NIST in-house research also increases by 16% to 447 million dollars. The budgets for all the ACI institutions have been increased considerably.

Table 2.2.1 shows a breakdown of the DOE Office of Science’s budget by area. Although budgets to all the areas have increased in 2009, those for ITER nuclear fusion — whose budget sharply declined once in 2008 — and facility construction have increased remarkably. It appears that the rapid growth of the DOE Office of Science’s budget has been due to the ACI.

Although the ACI-related budgets have greatly increased, comparing budgets for fundamental research with that for applied research shows that, although there has been a relative increase in fundamental research budgeting, it has not been as great, and that the budgets for developments and facility constructions are increasing.

It appears that the prioritized investments tend to go towards the budgets for the infrastructures related with the ACI institutions.

### 2.3 DOE Research and Development Tasks

The United States’ Department of Energy is a branch of government dedicated to “energy”; there are no such large ministries in Japan, besides Agency for Natural Resources and Energy. The mission of the DOE focuses on energy security and scientific and technological innovations. The department is composed of four R&D divisions, national defence, energy, environment, science, and the administrative division. The mission of the DOE’s Office of Science is to take responsibility for remarkable scientific discovery, deepening understandings of energy and materials, managing scientific tools to help advance the nation and the economy, and ensure the U.S. energy security. The administrative scope of the Office of Science is extremely broad, and it must involve itself in just about everything that has “energy” as a key word. One could say that everything the DOE does is related to “energy.” Naturally, this does not mean that the DOE has suddenly begun to promote energy research, rather, in these years, policies emphasizing resources and energy have meant that more efforts are being directed in these areas than before.

In line with the American Competitiveness Initiative (ACI), the DOE Office of Science announced its FY2007-FY2011 5-year Plan in October 2006 which set out the following strategic themes:

1. Energy security (promoting America’s energy security through reliable, clean and affordable energy);
2. Nuclear security;
3. Scientific discovery and innovation (promoting U.S. scientific discovery, economic competitiveness, and improving quality of life through innovations in science and technology);
4. Environmental responsibility (protecting the environment by providing a responsible resolution to the environmental legacy of nuclear weapons); and
5. Management excellence.

The concrete strategies have been set up based on these themes. Specific strategic goals for 3) Scientific discovery and innovation are as follows:

3-1) Scientific breakthroughs
- Achieve the major scientific discoveries that will drive U.S. competitiveness; inspire America; and revolutionize approaches to the nation’s energy, national security, and environmental quality challenges.

3-2) Foundations of science
- Deliver the scientific facilities, train the next generation of scientists and engineers, and provide the laboratory capabilities and infrastructures required for U.S. scientific primacy.

3-3) Research integration
- Integrate basic and applied research to accelerate innovations and to create solutions for energy and other U.S. needs.

There are many points of contact between these strategic themes and “materials science”: In 1) Energy security, breakthroughs are required in electric energy storage, superconductivity, bio-fuels, hydrogen storage and...
fuel cells, solar cells, advanced nuclear energy materials, and capture of \( \text{CO}_2 \) from existing fossil-fuelled plants. Significant science opportunities include the design and synthesis of materials exploiting nano-scale understandings; advanced computational science and predictive modelling of complex materials; catalysis and control of chemical transformations; and systems and synthetic biology for energy applications.

In 2) Nuclear security, breakthroughs are required in radiation resistant materials, innovative materials for safeguards and security, nuclear proliferation detection, remote sensing and analysis of radioactive/fissile materials and nuclear weapons, and modelling and simulation.

In 4) Environmental responsibility, molecular/atomic-scale science addressing the chemical natures of environmental processes; the integration of molecular biology and genomics techniques; the development of novel monitoring and measurement tools; chemistry and separations for radioactive waste; modelling, simulation, and scaling issues for environmental management are all important.

As the description of the DOE budget in Table 2.2.1 shows, within the Office of Science, the budget for Basic Energy Science (BES) is the largest, and within this, the portion of the budget for materials science is the greatest. This gives an indication of the importance of the contribution of materials science and its considerable responsibility.

2.4 Planned Provision and Utilization of Large-scale Research Facilities

The DOE strategy aims at achieving innovations through scientific discovery and the progress of deeper fundamental sciences; it does not seek to develop and build gigantic energy plants on a large scale. On the other hand, the DOE has adopted a clear strategy for effectively managed, large-scale shared-use research facilities that are unequaled overseas, in order to achieve significant scientific innovations. To achieve this goal, the DOE has issued a 20-year plan to systematically and totally establish large-scale research facilities, and has indicated the facilities that should be provided, in its publication “Facilities for the Future of Science” that divides these facilities into three priority groups: short-term, medium-term and long-term. For example:

1) Short-term priorities: ITER, UltraScale Scientific Computing Capability (USSCC), Joint Dark Energy Mission (JDEM), Linac Coherent Light Source (LCLS), protein manufacture and protein tags, rare isotope accelerators,

2) Medium-term priorities: linear colliding-beam accelerators, cellular analysis, Spallation Neutron Source (SNS), the target improvement,

3) Long-term priorities: improvement of the National Synchrotron Light Source (NSLS), high-intensity neutrino beams, improvement to the Advanced Light Source (ALS), upgrading of Advanced Photon Source, etc.

The publication includes a technical description of each of these facilities, future plans and associated budgetary measures.

In its line of thought for these scientific user facilities, it is almost of necessity that the DOE will decide to establish nano-scale research laboratories at these large-scale research facilities.

2.5 From Nanotechnology to the Environment and Energy ??

The National Nanotechnology Initiative (NNI) was established as a federal program in 2001 starting with six institutions: the National Science Foundation (NSF), the Department of Defence (DOD), Department of Energy (DOE), the National Aeronautics and Space Administration (NASA), the National Institute for Standards and Technology (NIST) within the Department of Commerce (DOC), and the National Institutes of Health (NIH) within the Department of Health and Human Services (HHS). The NNI program advocates world-class nanotechnology programs, creation of economic growth and employment, creation of products from new technologies, development of human resources and supporting infrastructures. Since 2001, the NNI’s budget has steadily grown. It has produced many outstanding research results, and the number of participating institutions has increased to 26. It appeared that the DOE (responsible for “energy”) at first did not see a close connection between “nanotechnology” and “energy,” and the first budget was about half that of the NSF. Nevertheless, from about FY2003 onwards, it seems that the DOE has started to promote the establishment of nano-scale research centers at the national research laboratories under its control. As a result, the NNI budget rapidly increased. The 2009 NNI budget related to DOE has grown 23.9% to 311 million dollars, while the NSF budget has increased by 2.1% to 397 million dollars.

Does this involvement of the DOE in the NNI mean that the DOE laboratories are trying to become nanotechnology research institutions? Or, that given the current global and political status where the environment and energy are viewed so seriously, there comes up a suspicion that the DOE’s adoption of an offensive stance backed by the ACI might signify that the focus of research has shifted from nanotechnology to energy. In fact, when discussing future plans, the question always arises of whether or not the “environment and energy” should come after “nanotechnology.”

In response to this question, the DOE policymakers appear to have given a clear answer. When the authors asked the question directly, they were told that it is not a matter of nanotechnology and energy competing against each other, in other words, it is not a choice between the two, but rather that “nanotechnology has been extremely important in the promotion of energy research and development to date, and we will emphasize it even more in future.”

Table 2.2.2 shows the areas in which the DOE links “energy” and the environment” and “nanotechnology”.

Although the attitude that nanotechnology is valuable in solving environmental and energy problems is an obvious one to have in the laboratory, when reflect upon attitudes in Japan, we see that the both subjects together have not been so promptly accepted at the same time, and in medium-term plans and research proposals we read such phrases as “necessity to avoid duplication of investments,” or “insufficient accountability.” In Washington D.C., the “multi-funding” approach has been adopted by the gov-
ernment whereby financial assistance is readily given (not earmarked for specific organizations) as long as the people and institutions that need it can carry out their mission more effectively. Also, the DOE is about to embark on an active program of education and training. For example, the NSF and the DOE play a partnering role within the federal government, but they are also friendly rivals. There would be constructive suggestions when we consider our future planning for research and development.

3. Nano-scale Research Facilities in DOE Laboratories

3.1 Nanoscale Science Research Centers (NSRCs)

The Nanoscale Science Research Center (NSRC), with their extensive and systematic arrangement, exemplifies the DOE’s positive stance in the field of nanotechnology. There are five Nanoscale Science Research Centers (NSRCs) in six DOE national laboratories (one of the Centers is jointly shared between two institutions), and their operations are controlled by themselves. As discussed in Section 2.4, the DOE runs the large national laboratories and has historically built and operated some of the world’s best large facilities and equipment, including synchrotrons, accelerators and neutron sources.

The new five Centers are located adjacent to these large facilities to take advantage of the complementary capabilities of these large scientific facilities so that the facility equipment can be used for research in the nanotechnology intensively.

The mission of the NSRCs is to:
1) Provide the research facilities for the synthesis and processing of nanoscale materials;
2) Supply specialized and unique tools and equipment that individual research institutions would find difficulty to construct and maintain, and provide the support staff for these;
3) Open the user facilities to all researchers, subjecting all themes to thorough peer review, and charge for private research;
4) Establish NARCs in DOE national laboratories having large facilities to provide the ability to measure and analyze materials.

The five DOE NSRCs make the maximum possible use of the extensive research facilities of the various national laboratories and work to cooperate and collaborate with them on projects. Each NSRC specializes in a different nanotechnology field, can use facilities throughout the U.S., and is capable of providing support for a very wide range of research and development.

Fig. 2.2.3 shows all the Basic Energy Science user facilities of the DOE’s Office of Science. The red text indicates a neutron source, the blue indicates a synchrotron radiation source, the green indicates electron microscopy, and the purple shows the location of a Nanoscale Science Research Center (NSRC).

Beginning with the establishment of the Center for Nanophase...
Chapter 2. Trends in Materials Research for the Environment and Energy

Materials Sciences at the Spallation Neutron Source (SNS) of the Oak Ridge National Laboratory, large research facilities and special equipment such as synchrotron radiation sources have been set up adjacent to or within the national laboratories. Table 2.2.3 shows the relationship among the national laboratories, their associated NSRC and the specialized research equipment that the laboratories have, as well as a summary of the area of specialization of each NSRC. By combining the NSRCs that can fabricate, measure and analyse nanoscale materials in the world-class laboratories that have unique large-scale research facilities, some truly innovative will be possible.

The FY2008 NRSC budget totalled $279.45 million, of which $122.33 million was earmarked for research associated with materials science, and $57.08 million went towards related research in other science fields, meaning that 64% of the NRSC budget was for research expenses. From the standpoint of placing importance on innovations, the NRSCs are aiming to become research platforms for corporate researchers.

Information about each NRSC, the details of its areas of specialization, research equipment, infrastructures, how to use its services and so forth is all available to the public and so will not be repeated in this paper.

The NRSC websites are listed below.

- Center for Nanoscale Materials=> http://nano.anl.gov/
- Center for Functional Nanomaterials => http://www.bnl.gov/cfn/
- Molecular Foundry=> http://foundry.lbl.gov/
- Center for Nanophase Materials Sciences =>http://www.cnms.ornl.gov/
- Center for Integrated Nanotechnologies= http://cint.lanl.gov/

3.2 Accountability and Peer Review

In the advancement of energy research, research decision-making (setting the direction), accountability and management will become even more important. Here, this section describes the DOE’s research fields, its setting of priorities, funding allocation, and decision-making concerning research themes, and in particular the process of accountability and peer review. The DOE’s approach to all of these permeates through to the administration of the “scientific user facilities” at the national laboratories. The DOE, in its use of public finding, places great importance of accountability, and widely uses the process of peer review by many academics in appraising the scientific content of research proposals. The DOE acts as an interface between societal interests and the institution's originality.

Prioritization of important research themes is decided through discussion at widely publicized open workshops that are attended by over 100 people. After hearing the opinions of about 2,000 researchers, the DOE sets priorities for the topics to become involved with, selects strategically important fields (by top-down), clarifies the remark points and prepares a draft budget for the important fields of research and budget allocation. Next, each research theme is subject to peer review; this is at the heart of all DOE decision-making. On the other hand, if a new field (research theme) emerges during the peer review of the research project applications and is considered to be particularly important, then the process has the flexibility to review the size of the strategic importance budget (program size) so that funds can be allocated for that new theme. The DOE decision-making process thus emphasizes peer review outcomes as feedback.

Numerous workshops are held to discuss NSRC facility construction and operation and to debate their directionality. This ensures that user needs are properly taken into consideration. The DOE approach is characterized as carrying out exhaustive workshops and peer reviews.

For example, the Molecular Foundry at the Lawrence Berkeley National Laboratory gives assistance to achieve a continuous process, from the pursuit of principles to eventual commercialization. Before this assisting system began, numerous workshops had been held to discuss the methods of operation. After the assistance begins, the selection of the research themes is made based on peer review. The operators of the Molecular Foundry solely decide matters of the environment, health and safety (EHS Review); the key to whether or not a project goes ahead is held
by outside scientists. This policy is generally common to all the DOE scientific user facilities.

One can say that the assistance to the research themes, selected by the process of listening carefully to the opinions of people outside the program and scientifically evaluated through peer review, is a free service — and is the DOE way.

4. Expectations Towards and Responsibilities of Science and Technology in the Environmental and Energy Fields

Under the global situation surrounding the environment and energy in recent years, it has become a worldwide recognition that the expectations of both governments and society that science and technology (research institutions and scientists) will come up with solutions are growing. More than ever before, we need to take a strategic approach to dealing with the environmental and energy problems. In the nanotechnology and other fields, the usual approach is to view the science and technology as being the source of a nation’s economic growth and international competitiveness, or to aim for innovations by creating knowledge. And serendipity may be allowed while one is searching for a technical breakthrough. Nevertheless, participating in the impending political challenge of “securing energy sources and creating a sustainable society while attempting to suppress global warming and reducing the environmental negative impact” probably requires more strategic and harmonious approaches, rather than going on the offensive, and also requires an organizational response while dealing with the politics. It is likely that the expectations placed on national research institutes as well as their responsibilities will increase.

Future forecasts suggest that energy demand will likely continue to increase for the time being. Whether levels of emissions of greenhouse gases will reach constant levels or even begin to fall, decades into the future, or whether a “happy solution” for the mankind to these problems exists or not — nobody knows for sure. Finding the solutions is being left to the science and technology of the future. If our current safe, secure and affluent lifestyles are not greatly scaled back, there may be no other ways to overcome these environmental and energy problems other than by progressing science and technology, and the people who are responsible for this science and technology will have great hopes and responsibilities placed on their shoulders.

As one of the possible energy technologies to secure the energy supply and to reduce the emission of greenhouse gases, nuclear power and technologies such as ones to collect and store carbon have recently become a focus of attention, along with the promotion of the development of energy conservation and renewable energy sources. Finally, it should be stressed that that almost all the environmental and energy-related research and developments are closely linked to materials science and technology.

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Chapter 3. Electron Energy Materials

3.1 Overview

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1. Chapter summary

Electron energy materials are semiconducting materials that are able to directly convert the energy of electrons into electrons, light, heat and other forms of energy. What makes electron energy materials different from ordinary electronic materials is that they are semiconducting materials that are used for energy devices. Electron energy materials are attracting a lot of attention for their applications in renewable energy and their potential to make energy use more efficient, and are seen by many being advanced materials that hold the key to solving environmental and energy problems. Materials that convert mechanical energy into electron energy or vice-versa will be introduced in Chapter 6 that discusses mechanical response materials.

Section 3.2 of this Chapter will discuss solar cell materials that convert light energy into electron energy. People all over the world are interested in these materials that can produce electrical energy from the inexhaustible supply of sunlight, and the competition between developers is fierce. The current research trends and technical themes can be summarized and classified into the following categories: silicon (Si), CIGS, dye-sensitized, organic thin-film, and quantum dot systems.

Section 3.3 will look at LED materials that convert electron energy into light energy. Japan leads the world in the development and application of LED materials, and this section will discuss current themes from a technical perspective.

Section 3.4 will discuss (power) electronic materials that convert electron energy to electron energy. Electronic materials are used in devices that are an intimate part of our daily lives. Section 3.5 will use the PC and digital consumer electronics as examples and give an overview of the current situation and the future, from the viewpoint of the environment and energy.

Section 3.5 will touch on thermoelectric conversion materials that can convert heat energy into electron energy and vice-versa, and will discuss their applications as well as present and future technical issues. Compared with other electron energy materials, thermoelectric conversion materials will come into their own more in the future.

2. Key words from material science

All the electron energy materials discussed in this Chapter are semiconductors that have a band gap. To organize the material science factors that determine the conversion efficiencies of solar cell materials, LED materials, (power) electronic materials and thermoelectric conversion materials, the issues important for the raising of efficiency are listed under the “key items” and areas where they apply are listed under the title “keywords.” Regardless of whether the material is organic or inorganic, these are abstracted material science topics. The results are shown in Table 3.1.1.

There are six “key items”: material structure control,” “impurity control,” “band gap control,” “conduction mechanism control,” “space-charge layer control,” and “heat management.” In this Chapter, we will attempt to explain each type of material in terms of the factors in the “key items.” This is to provide a wide-ranging view of different types of materials and scientific fields. The keywords used in this paper are shown in bold.

<table>
<thead>
<tr>
<th>Key items</th>
<th>Keywords</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Material structure control</td>
<td>Atomic bonding and structure, superlattice structure, molecular structure, molecular orientation, quantum structure</td>
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<tr>
<td>2) Impurity control</td>
<td>Purity, crystal defects, distribution control, configuration control</td>
</tr>
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<td>3) Band gap control</td>
<td>Solid solution, elastic strain, degeneration, transformation, chromic, polarization</td>
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<td>4) Conduction mechanism control</td>
<td>Band conduction, hopping conduction, ballistic conduction, strong correlation</td>
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<td>5) Space-charge layer control</td>
<td>p-n junction, Schottky junction, electric double layer</td>
</tr>
<tr>
<td>6) Heat management</td>
<td>Heat transfer, phonon conduction, thermoelectric correlation, coherency</td>
</tr>
</tbody>
</table>

Table 3.1.1 Keywords in Chapter 3
3.2 Solar Cell Materials

Chisato Niikura
Advanced Electronic Materials Center, National Institute for Materials Science

1. Fundamentals of solar cell materials

Solar cells are devices that convert directly the energy of light into electrical energy by utilizing the light absorption, photoconductive effect and photovoltaic effect of materials. The most typical of these are crystalline silicon (Si)-based solar cells. Structurally, these are pn-junction diodes that have a large surface area to capture sunlight. Fig. 3.2.1 illustrates the principle of the pn-junction solar cell. Light absorption within the semiconductor creates electron-hole carrier pairs. The internal electric field at the pn-junction causes a drift effect which polarizes the carriers. The polarized carriers are collected at the electrodes, which causes a photoelectromotive force. The increase in conductivity of a semiconductor due to an incident light, $\Delta\sigma_{\text{ph}}$, can be expressed by the following equation:

$$\Delta\sigma_{\text{ph}} = \varepsilon \mu_e \tau_e + \mu_h \tau_h,$$

where $\mu_e$ and $\mu_h$ are the mobility of electrons and holes; $\tau_e$ and $\tau_h$ are the lifetime of electrons and holes, respectively, $g$ is the generation rate of photo-generated electron-hole pairs in unit time, $e$ is the elementary electric charge. The absorption of light in a semiconductor occurs basically by transition of photo-excited electrons from the valence band into the conduction band. Therefore, incident light with photon energy higher than the energy band gap is absorbed. Fig. 3.2.2 shows the absorption coefficient spectra of the semiconductors used for prevailing solar cells. The performance of a solar cell is also closely related to the band gap. The smaller the band gap, the greater the short-circuit current density and the lower the open-circuit voltage. At a band gap of some 1.4 eV where both of them attain a proper balance, the theoretical limit energy conversion efficiency (i.e., ideal solar cell efficiency) of a single-junction solar cell for the solar spectrum is obtained around 30%, which is the maximum value.

2. Research trends

World solar cells market has rapidly expanded in the last few years, propelled by environmental concerns, skyrocketing crude oil prices and government policies. At present, bulk crystalline Si-based solar cells, such as monocrystalline Si solar cells and polycrystalline Si (poly-Si) solar cells, comprise 90% of the market. However, market growth has resulted in a Si raw material shortage, and there is an urgent need to develop manufacturing technologies for mass-production of solar-grade poly-Si at low cost.

Because of the shortage of Si raw materials, material saving thin-film solar cells including thin-film Si-based solar cells and thin-film Cu (InGa) Se2 (CIGS) compound solar cells, have attracted much attention as the next generation solar cells suitable for popularization of photovoltaic system. They have also the advantage of requiring lower energy input and causing lower levels of greenhouse gas emissions in their manufacture. Researches into thin-film Si-based materials have been promoted in Japan as part of national projects “Sunshine Project” (from 1974) and “New Sunshine Program” (from 1993) that were prompted by the Oil Shock of the 1970s. Studies to elucidate the mechanism of photo-induced deterioration phenomena of amorphous Si (Staebler-Wronski effect) have been ongoing. Actually, researchers are trying to control nanostructure associated with this effect by controlling film growth process. The conversion efficiency has been improved by techniques that include using amorphous SiC in the p-type window layer of the pin structure, light confinement techniques and tandem-junction structure. Recently in Japan, amorphous Si cell / microcrystalline Si cell tandem junction modules with a conversion efficiency approaching 12% have been commercialized. For development of multiple junction solar cells, researches on new materials such as microcrystalline SiGe and microcrystalline SiC are underway. Flexible...
film type solar cells modules have also recently been commercialized in Japan. Researches into thin-film CIGS compound materials have been preceded by the U.S. and Germany. Mass-production has recently started in Japan as well despite the difficulty in manufacturing a uniform compound film on a large surface area. CIGS compounds have been developed by adding Ga to CIS compounds that have a small band gap of 1.0 eV. Altering the In1-xGax, composition enables band gap control within the range of 1.0 to 1.7 eV and yields a thin-film with a graded band gap structure that may enable higher efficiencies. ZnS and InS compounds have been developed as substitutes for the CdS buffer layer, the problem of which is cadmium toxicity. CdTe compounds have a band gap of 1.5 eV, a high absorption coefficient, and can be manufactured using an energy-conserving process. These may prove to be excellent materials for solar cells. There are many examples of research in this area, although this has not spread to Japan due to the problems associated with Cd use.

Researches have been carried out into dye-sensitized solar cells and organic thin-film solar cells as future solar cells that can be mass-produced at low cost. Since the invention of dye-sensitized solar cells, or Grätzel cells, in 1991, research and development has forged ahead actively worldwide. Over the years, various researches and developments have been underway, for example, to replace electrolyte liquid by a solid one to improve durability, to expand the surface area, and to increase the conversion efficiency by developing high-performance dyes. Development of plastic flexible cells and battery cells has also been carried out. Concerning organic thin-film cells, many researches have been carried out since the turn of the 21st Century, particularly in Europe and the U.S. Initially, Schottky junction cells were fabricated, but with the application of organic EL technology, p-n hetero junction cells have been created.

Subsequently, the research has been progressed by the mass-synthesis of n-type organic semiconductor fullerences. Development of bulk hetero junction structure composed of nanolevel p-n junctions that increase the molecular p-n junction interface has improved the conversion efficiency of the cell. The more widespread use of soluble conjugated conducting polymers has also made a major contribution to development of research. Recently, a conversion efficiency of 6.5% has been achieved in a tandem junction solar cell.

With a different design concept to the low-cost solar cells described above, development of super-high-efficient solar cells that seek to reduce electricity costs through higher efficiency is also targeted. There are approaches for applying III-V group compound (CaAs, InP, etc.) solar cells developed for space use because of their high radiation resistance to terrestrial use in multi-junction structure and solar concentrating system. Research is also progressing on quantum-dots type solar cells that have a theoretical conversion efficiency of over 60%. Recently, a conversion efficiency of 8.5% has been achieved in Japan.

Owing to a superlattice structure composed of laminated quantum-dots layers placed between p- and n-type layers, minibands could be created, which enables absorption of light over a wide range of wavelengths. Research in this area has just started, and the verification of the principle is required.

3. Applications in the environment and energy fields

Solar cells attract attention as renewable energy source with the potential to solve problems of energy resource and global environment. Solar cells work by the energy of sustained and inexhaustible sunlight, without consuming fossil fuel and releasing greenhouse gases. They are silent, having no moving parts. They can be used as distributed energy source. The biggest obstacle preventing the more widespread use of solar cells to compete with conventional energy sources is their high cost. Overcoming of various technical problems will enable low cost mass-production of high efficiency solar cells and enable their widespread unlimited use. The Japanese government has proposed a policy of supplying 10% of the nation’s domestic electricity by photovoltaic energy by the year 2030.

4. Material science development challenges

There are a range of material science issues for each material that need to be overcome.

1) Crystalline Si-based materials: The development of technology for the mass-production of poly-Si at low cost.
2) Thin-film Si-based materials: Control of the photo-induced deterioration in amorphous Si. Control of defects and impurities in the i/p interface. Development of new materials for multi-junction solar cells.
3) Thin-film CIGS materials: Development of a substitute for the rare metal In. Development of new wide-gap materials such as S-based or Al-based ones for multi-junction solar cells.

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For readers who want to find out more about solar cells:  
2) Hakumaku Taiyo Denchi no Kaihatsu Saizensen (The Front Line in the Development of Thin-Film Solar Cells) (Japanese language), NTS Inc. (2005).
3.3 LED Materials

1. The operating principle of LEDs and the materials features

A p-n junction diode is formed from an n-type semiconductor with electron conducting properties and a p-type semiconductor with hole conducting properties. Minority carriers are injected across the junction in a forward direction, resulting in the recombination of electrons and holes. If energy is released in the form of light at this point, then the diode can be used as a light emitting diode (LED). Fig. 3.3.1 shows the structure of an LED. Essentially, the LED is a p-n diode, but with modifications near the light emitting layer to improve the efficiencies of recombination luminescence and the optical output. LEDs have a chip size of about 300 microns, where a current ranging from several dozen to several hundred mA is consumed. The driving voltage varies, depending on the LED material, but is in the range of about 2 to 4 volts. Compared with a conventional incandescent light bulb, the energy efficiency of an LED is far greater, and could be as high as 70% or more (the external quantum efficiency of a blue-light LED) with structural optimization. Nowadays, with the drive to conserve energy, applications for LEDs are being found in various kinds of indicators of electrical equipments, traffic lights, Christmas decorations and other uses. The key to use in these kinds of applications has been the success of the blue LEDs. LED “light bulbs” that use white LEDs and are as bright as conventional 40- or 60-watt bulbs are already being marketed. LEDs will also find greater use in fields where they can take advantage of their superior monochromatic qualities.

The first thing to consider in an LED material is the energy band structure of electrons. The wavelength of the emitted light depends on the band gap. The luminous efficiency is determined by whether or not the phonon process is required for the recombination of electrons and holes (whether the semiconductor is a direct or indirect transition type). At the practical application stage of an LED, the impurity doping techniques (to modify the electronic properties of the semiconductor), the level of impurities and the control of crystal imperfections are important factors. Fig. 3.2.2 shows an example of a plot of the external quantum efficiency in charge injection light emission vs. peak wavelength. Basically, the wider the gap, the lower the luminous efficiency. This is because trap levels are easily formed within the gap accompanying crystal imperfections, recombination luminescence is hindered, and the deep impurity levels common to wide-gap materials become a serious problem, causing increased losses due to electrical resistance.

2. Research trends

The development of gallium nitride ultra-violet LEDs used in blue light diodes, as well as deep ultra-violet LEDs that use wide-gap materials, are still in the research stage however it is already attracting a lot of attention. Wide-gap materials include gallium-aluminum-nitride, aluminium-nitride, boron-nitride and diamond. Ultra-violet LEDs emitting light with wavelengths in the 355 to 375 nm range have already been partially commercialized and are used in paper currency recognition devices, air purifiers and other devices. It is hoped that the deep ultra-violet LEDs, with tunable wavelengths and abilities to kill bacteria, will be used for a wide range of devices, including high-quality white-light sources and the next generation of high-density data storage. At present, the external quantum efficiency of these LEDs at a peak wavelength of around 260 nm is no more than 1%, and near 240 nm it is very low –around 10⁻⁴ %. Nevertheless, diamond LEDs utilize light that is emitted by the recombination of free carriers.
excitons, and it has been proposed that long-lived excitons characteristic to high quality diamond can drastically improve the internal quantum efficiency. This may make it possible to achieve an external quantum efficiency of 10% in an LED that emits deep ultra-violet light of a 235 nm wavelength. Researchers have also confirmed that hexagonal boron-nitride (h-BN) crystal can emit laser light with a wavelength of 215 nm through electron beam excitation. Since this is a flat-layer crystal, it is different from ordinary crystals, and further research will be conducted into the control of its electric conductivity through doping and other techniques. If charge injection procedure has been available in solid-state junction structure with h-BN, then this may turn out to be a material with huge potential.

The “green gap” is another problem that besets LEDs as there is no material that can be used to generate pure green light (555 nm) at high efficiency. Fig. 3.3.3 shows the emitted light wavelength dependency of the external quantum efficiency of LEDs that emit light in the visible wavelengths. The visibility of human eyes has maximum value for green colour and people do not sense the dimness of a green light LED. However, low efficiency of green LED can become a problem when attempting to create white light out of the three primary colours. At present, the highest efficiency achieved is around 5 %, which is at least an order of magnitude less than for red or blue LEDs. The development of a highly efficient green LED is an important task for scientists.

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For readers who want to find out more about LED materials:
1) Hakkou Daiodo to sono Ouyou (“LEDs and Their Applications”) (Japanese language), Sangyo Tosho Publishing Co., Ltd. (1988).

3. Energy conservation, environmental protection and views of the future

Since the arrival of practical blue LEDs, the range of applications of light-emitting diodes has greatly widened. Illumination by LEDs has the advantages of high efficiency and long bulb life. LEDs are being used in more and more energy conserving products. In some products using LED, energy consumption level is far below the target of the Kyoto Protocol which requires the energy consumption level of one-fifth of the conventional devices. LED “light bulbs” have a service life that is some 20 times longer than conventional light bulbs and some 5 times longer than fluorescent tubes. (Some LED lights have a lifespan of more than 50,000 hours.) LEDs are certainly a perfect light source for the “Eco-Age” and will be very useful in reducing the impact on the environment. They also excel as safe substitutes for fluorescent tube lights as they do not contain mercury. In future, LEDs will become more widely used in different applications that will use their properties of being able to provide monochromatic light without heat. In the field of medicine, super-small endoscopes that use LEDs as a light source are very effective in reducing patient discomfort. On the other hand, organic EL panel research is making amazing progress, and is competing with other forms of illumination — although LEDs are more reliable at present. It is hoped that ultra-violet LEDs will be used in highly efficient data recording, detection of unwanted bacteria, in products from gas monitors to sterilizers and advanced information networking, and will help make society a safer, more secure place by enabling the creation of products that use less power and take up less space.
3.4 Materials for Electronic Products

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1. Personal computers, the environment and energy

When you hear the word “electronics,” the first thing that comes to mind is probably the personal computer (PC). The author remembers a PC called the “Mi-Com” (Micro Computer) that appeared on the market in Japan when he was a junior high school student. He fondly remembers reading through a catalogue of a calculator that sported an 8-bit CPU (central processing unit), saving up his pocket money… those were the days. Twenty years ago, when he was a 4th-year student preparing his graduation thesis, the author was permitted to use up to 2.7 MB of memory on the university’s large scale computer installed in the information-processing center. Unfortunately, this was not enough — no matter what he did — and so he was granted special permission to use about 4 MB of space. That 4 MB is only about the size of a personal computer CPU cache today.

Compared with the large scale computers of 20 years ago, think about the PCs of today, with their memory capacities a 1,000 times greater and all their fantastic processing power… Let’s look at them in terms of energy consumption. As you know, today’s PC have fans to keep them cool, and if you have even worked with a laptop on your knee, you will know that they can get so hot that you would think you would burn yourself. Lets compare the heat of a typical CPU with an Intel® (Note a) CPU 1). First of all, the Pentium® (Note a) D Processor 930 (CPU clock speed of 3.0 GHz) has a design thermal output (Intel® thermal design power (TDP) value) of 65 watts. By comparison, the Core™ 2 (Note a) Duo Desktop Processor E8400 that has a similar clock speed of 3.0 GHz also has a TDP of 65 watts. Unfortunately, the author does not know which indices are the best for comparing the performance of arithmetic and logic units of PCs, but comparing these two CPUs reveals that while they both have the same heat output, the newest one has a higher calculating performance. In other words, a saving of energy per unit processing of CPU has been achieved. This trend towards greater energy conservation is the result of several factors that include newer PCs having newer types of materials inside them, the development of micro-fabrication technology in the manufacture of CPUs with the result that a lower operating voltage can be used.

Development of PCs, electrical and electronic goods that do not use toxic materials or poisonous elements is another trend in the development of new products. One clear example is the use of lead-free solder. When electronic devices that contain circuit boards that have been soldered conventionally are exposed to acid rain, the lead leaches out and can lead to soil contamination of industrial waste storage site. The RoSH (Restriction of Hazardous Substances) Directive 2) that we often hear about nowadays is one example of regulations to control the use of hazardous substances and toxic elements in manufactured products. Lead in particular is strictly controlled. With the exception of lead sinkers used in fishing, lead-acid batteries and other products where there are no suitable substitutes, the use of lead and lead compounds is strictly controlled. RoSH directives are applied not only to solder and electronics but provides a wide range of environmental protection measures.

In recent years the phrase “urban mining” 3) has entered the language. Personal computers and other electronic devices have gold contacts because this metal does not tarnish and is such an excellent electrical conductor. Even though each PC or mobile phone only contains a tiny amount of gold, this all adds up to quite a large amount of this precious metal. This means that our cities have valuable resources in their rubbish dumps. When thinking of the global environment as a whole, it is extremely important to recycle PCs and other electronic goods. Already, the movement in this direction has begun.

2. Digital home appliances and the environment

In the electronics field, developments among digital home appliances have caught a lot of attention. Good examples include flat-screen televisions, video cameras and printers. These use all kinds of electronic components, for example, the lens-driving

Note a Intel®, Pentium® and Core™ are registered trademarks of Intel Corporation.
mechanisms of video camera auto-focus systems, or the ink ejecting mechanisms of inkjet printers. These components use piezoelectric elements that expand and contract when a current is passed through them. PZT (lead zirconate titanate) is the name given to a special ceramic material that is a typical piezoelectric material. This expanding and contracting quality of PZT is put to use in motors, valves, speakers and other components. Unfortunately, lead is one of the key ingredients in PZT. Regulations like the RoHS Directive introduced earlier mean that lead-free piezoelectric materials are sought, but no piezoelectric material has been developed so far that has sufficient performance to be a viable PZT replacement. Despite the RoHS Directive, the use of PZT as a piezoelectric material is permitted even though it contains lead. In the meantime, the development of lead-free piezoelectric materials is advancing rapidly.

Development of electronic paper technology is progressing towards the ultimate goal of a paperless society through IT promotion. It is hoped that electronic paper technology will develop materials that can be bent and curved like paper, that have a surface like a TV screen whose contents can be easily changed, but can display images without using a lot of power. Many companies in Japan have already started to sell such products. In the same way that the memory stick has taken over from the floppy disc, we are about to see the day when electronic paper takes over from paper as the medium of information communication. The author does not have any information at hand about how the switch from floppy disc to memory stick and from paper to electronic paper has impacted on carbon dioxide emission assessment or industrial waste assessment. Nevertheless, the trend to switch over to these kinds of rewritable data media that can be reused and not thrown away is expected to help lower energy consumption and the environmental impact.

3. Summing up

The author has introduced some simple examples of the work that is being done in the electronics field to reduce the environmental impact and conserve energy. As discussed in the example of PZT materials, there are many materials containing toxic elements and compounds that we knowingly continue to use as there are no viable substitutes. The earlier chapter on LEDs mentioned that fluorescent lamps use mercury — a well-know toxic heavy metal. Unfortunately, we don’t have any other kind of lighting that has the energy efficiency, environmental performance or design aesthetics to replace existing fluorescent lighting — which is why we continue to use it. Similarly, in the real world we have to find a trade-off between hazard, environmental impact and economic efficiency to decide the value of a product.

Like the example of the solder, the author hopes that electronic materials that place a lower impact on the environment will be developed, along with electronic devices that will use them. Maybe we need to reconsider whether our contemporary society, in which people can use game machines or personal computers that have the processing power of super computers of 20 years ago in their homes, really means we have achieved true affluence.

The author was assisted in the writing of this paper by Kenji Matsumoto, a NIMS junior researcher.

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   http://www.intel.com/
2) The Organization for Small & Medium Enterprises and Regional Innovation, JAPAN homepage
3) NIMS press release
4) Ceramics, The Ceramic Society of Japan
5) For example, M. Omodani, Kami e no Chosen Densi Peipaa (Electronic Paper Challenging Ordinary Paper) (Japanese language), Morikita Publishing Co., Ltd.
1. Basics of materials

Thermoelectric energy conversion materials (thermoelectric materials) are a topic of interest for their ability to make direct energy conversion between heat and electricity. This conversion occurs because the abundant carriers within the material transport thermal energy. Thermoelectric materials generally possess electrical properties that are somewhere between those of metals and semiconductors, and are known as “thermoelectric semiconductors.” The carrier concentration within thermoelectric materials (in n-type materials the carriers are electrons (-), and in p-type materials the carriers are electron holes (+)) ranges from $10^{25}$ to $10^{27}/m^3$. This is midway between the carrier concentration in ordinary silicon semiconductors ($10^{21}$ to $10^{22}/m^3$) and that in metals ($10^{27}/m^3$ or higher).

Thermoelectric energy conversion is reversible. When a thermoelectric material is subjected to a temperature difference, an electrical potential difference is generated between both sides of the material; conversely, when an electric current is passed through a thermoelectric material, one side of the material becomes exothermic and the other endothermic. Thermocouples for temperature measurement are examples of thermoelectric materials in which the voltage generated between both ends of the thermocouples is converted into the temperature.

Thermoelectric materials are used in the form of a thermoelectric energy conversion element, made up of a combination of a p-type and n-type materials. Fig. 3.5.1 shows the principle of thermoelectric energy conversion. The performance of a thermoelectric material is expressed by the figure of merit $Z (1/T)$ and derived using the following equation \[ Z = \frac{S^2\sigma}{\kappa} \] (1)

The figure of merit expresses the energy conversion efficiency when there is a temperature difference of 1K between both ends of the material. $S$ is the Seebeck coefficient ($\mu V/K$), $\sigma$ is the electrical conductivity ($S/m$), and $\kappa$ is the thermal conductivity (W/Km), $\kappa_c$ is expressed as the sum of the carrier component $\kappa_c$ and the lattice component $\kappa_p$.

2. Research trends

To make the figure of merit larger, you require a high Seebeck coefficient and electrical conductivity, but low thermal conductivity. Unfortunately, apart from the lattice component of thermal conductivity all the other factors are functions of the carrier concentration, and it is difficult to independently control the numerator and denominator of Eq.(1). As the carrier concentration increases, the Seebeck coefficient decreases and conversely, the electrical conductivity and the carrier components of the thermal conductivity increase. Each thermoelectric material possesses the characteristic optimum carrier concentration.

Fig. 3.5.2 shows the temperature dependency of the dimensionless figure of merit $ZT$ (T is absolute temperature) of developed thermoelectric materials for thermo-modules (highlighted in grey) and developing materials.

Examples of developed materials that have the small lattice components of thermal conductivity include heavy metal alloys such as Bi-Te, Pb-Te and GeTe-AgSbTe$_2$ based alloys (TAGS), and solid solutions such as Si-Ge systems. Scientists have recently found that within crystal structures there are cage-like struc-
tures, and if these cages are filled with large atoms, the thermal vibrations of those atoms drastically reduce the lattice component of thermal conductivity. Studies, chiefly in the United States, have focussed on skutterudite (shown in Fig 3.5.2 as p-CeFe₄Sb₁₂), whistler and clathrate materials.

In Japan and in the European Union, research is focussing on different materials, including Fe-Si, Mg-Si and Mn-Si based compounds. These have the advantages of being safe and being made from abundant raw materials. From the second half of the 1990s in Japan, research into Na-Co-O, Ca-C-O based and other strongly coupled oxides began. These materials have a Perovskite crystal structure consisting of alternating conducting and resisting layers, and are characterized by having a similar carrier concentration to metals and high Seebeck coefficients. Since the start of the new century, research, chiefly in Japan, has begun into polyanthiophenes and other organic polymers.

3. Applications in the environment and energy fields

3.1 Thermoelectric power generation

The efficient use of energy — making sure that you do not waste any of it — is important not only to energy policies but also to help reduce our impact on the environment. Thermoelectric power generation was originally developed to be a power source for use in outer space, the military and remote locations. Scientists are now looking into its applications in industrial plants, incinerators, boilers, automobiles and other heat sources to enable the generation of power from recovered waste heat. This power generation has the advantages of being compact, without any moving parts, silent and maintenance free.

3.2 Thermoelectric cooling (Peltier cooling)

Fig. 3.5.3 shows an illustration of a laser package for optical telecommunications as an example of how thermoelectric cooling is assisting in energy conservation and technological innovation by enabling precise temperature control which in turn makes it possible to maximise system efficiency. Both the transmitter and exciter components of the semiconductor laser package are cooled by Peltier elements (size: several mm square), to enable wavelength division of the laser light so that a large amount of data can be transmitted.

![Thermoelectric cooling module](image)

Fig. 3.5.3 Semiconductor laser package for high-volume optical data communication

4. Challenges in material science

At present we need materials that have a dimensionless figure of merit ZT equal to or greater than 2 for thermoelectric power generation and CFC-less cooling to become commonplace in society. In the last 10 years, research has attempted to increase this figure and has focussed on the relationship between material structure (including cage-like structures in crystals, substances with layered structures, and organic polymers) and thermoelectric performance.

From the mid-1990s, research, mostly in the U.S., has been conducted into creating quantum structures. This work has been based on theoretical predictions that if the dimensions of conductivity within a material are reduced by nano-dots, thin-film layers and other structures, then the Seebeck coefficient of that material can be greatly increased. Although scientists have yet to prove the validity of this theory, there have been reports that thermal conductivity has been reduced by at least a half, and that a ZT figure of greater than 2 has been achieved.

Material science researchers will have to grapple with the following issues.

1) A tie-up with computer science for study of atomic and molecular structure so that band gap control (already achieved through solid solution formation, distortion, doping) can be further improved.

2) There are many types of thermoelectric materials whose mechanisms of conduction need to be clearly understood.

3) Thermoelectric performance is studied in relation to average material structure; however, research that focuses on specific structure such as nano-particle dispersion (including quantum structure) is required.

4) Material research always uses raw materials of high purity; however, it is not clear how pure raw materials need to be.

5) The stability of the electrode on the hot side is the key to thermoelectric power generation. The development of electrodes that have both stable ohmic contact and contact strength is essential.

6) We need element-building technology that we can apply to a wide variety of device sizes and shapes.

References


For more information on thermoelectric materials,


Chapter 4. Chemical Energy Materials

4.1 Overview

1. Introduction

Chemical energy considered in this chapter refers to energy obtained in the form of heat and electricity through chemical and electrochemical reactions. This section will provide explanations regarding functional and structural materials for generating and storing this energy.

Energy obtained from fossil fuels is also a form of chemical energy resulting from combustion. However, this process generates carbon dioxide which is a greenhouse gas. This chapter looks into hydrogen (4.2) as a fuel which produces only water and no carbon dioxide when combusted. Furthermore, photocatalysts (4.3) have been categorized as chemical energy materials in this chapter since they make use of electrochemical reactions by electrons and holes generated by light (it is called “photo-chemistry” including effects of light). Fuel cells (4.4) and secondary cells (4.5), as their designation as 'cells' suggests, generate (fuel cells) and store (secondary cells) electrical energy by means of electrochemical reactions.

Moreover, chemical and electrochemical reactions can cause materials to lose some of their characteristics as functional and structural materials. Such degradation indicates corrosion; thus corrosion-resistant materials (4.6) are needed in overcoming this problem.

2. Keyword from materials science

Because chemical energy is a form of energy obtained through chemical and electrochemical reactions, it is vital to acquire an understanding of the reactions that comprise the driving force. Even if the driving force is substantial, if interfacial reactions cannot be prompted easily, or if they do not occur uniformly, energy cannot be tapped efficiently. If battery cells are employed, the electrical current flows through external electrical cables and loads, but needless to say, it also flows through electrodes and electrolytes inside the battery cell. Therefore, unless there is sufficient transport of electrical charges that bear the current in electrodes and electrolytes, the current cannot be extracted efficiently. Also, since chemical energy can be stored as fuel (hydrogen) and as electrical charges, methods and materials for storing greater volumes of this energy must be examined.

Conversely, with regards corrosion-resistant materials, the driving force may be minimized or else the material can be passivated to inhibit the occurrence of interfacial reactions.

Table 4.1.1 Keywords in Chapter 4

<table>
<thead>
<tr>
<th>Items</th>
<th>Keywords</th>
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<td>2. Interfacial reaction</td>
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<td>3. Uniformity</td>
<td>Reaction area, localized corrosion</td>
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<td>4. Transport</td>
<td>Electrode conductivity, electrolyte, diffusion, electrophoresis</td>
</tr>
<tr>
<td>5. Storage</td>
<td>Ion storage, hydrogen storage, pseudocapacity, electric double layer</td>
</tr>
</tbody>
</table>
1. Hydrogen and hydrogen energy

Hydrogen has the following characteristics; these characteristics embody both the appeal of hydrogen as an energy carrier as well as its drawback as a cause of problems to be solved.

- It rarely exists on earth in the form of a simple form of H2 molecule.
- The boiling point is -253 °C, and is second lowest next only to He.
- It reacts with many substances – explosively with oxygen.
- It allows direct extraction of electrical energy.
- It is absorbed by some metals (Group 2 to 5 elements, Pd).
- It is the smallest atom and diffuses quickly inside solids.

Figure 4.2.1 shows the flow of procedures from hydrogen production to energy use. Hydrogen must be produced by in one way or another from raw materials. Before energy can be extracted, it must undergo processes such as production, storage and transportation. Therefore, there are still numerous technical issues to be addressed in materials associated with hydrogen.

This paper reports on reforming catalysts and hydrogen separation membranes as materials for hydrogen production. Also, with respect to hydrogen storage materials, this paper will focus mainly on substances that will allow for storage in solid form and will exclude hydrogen production photocatalysts from the discussion to be dealt with in section 3 in this chapter.

2. Research trends

2.1 Hydrogen production materials

Hydrogen production catalysts

At present, most of the available hydrogen gas is produced from natural gas and fossil resources via reforming processes. Catalysts play a key role in reforming reactions; Ni-based alloy is used for methane reforming and Cu is used in methanol reforming. Although these techniques are now established industry practice, Tsai et. al. recently discovered an intermetallic compound which offers exactly the same catalytic functions as Cu by way of a guidance principle called valence band control. It was conventionally believed that functions of a catalyst were determined by the state of electrons on the microparticle surface of the catalyst metal or on the interfacial surface between the support medium and the metal microparticle. However, this result by Tsai reveals that, in actual fact, the electron state of the bulk played a key role. This finding raises expectations for major advancement in materials for the catalyst field.

Hydrogen refinement materials

Hydrogen is normally refined using the PSA method subsequent to reforming and shift reactions which require large-scale facilities. For this reason, membrane separation has recently attracted greater attention as a technique for making possible energy-efficient, compact system designs. Hydrogen separation membranes can largely be divided into two types – porous and non-porous membranes. Porous membranes facilitate separation by exploiting the differences in speed of the gas molecules permeating through the pores. The separation coefficient in porous membranes is around 300 for polymer membranes and can reach as high as 5000 using inorganic porous membranes depending on the type of gas. In contrast, metallic membranes do not have pores; they utilize the process of solid solution and diffusion into the metal lattice by hydrogen atoms that have dissociated on the metal surface. Consequently, if one choose a metal with high diffusivity and high solubility of hydrogen for the membrane, large volumes of hydrogen can be permeated and virtually infinite degrees of separation coefficient can be attained. Only Pd alloys have been used in actual hydrogen separation applications to date. Recently membrane materials using non-Pd alloys such as V and Nb alloys with BCC structures have been developed. Japan is leading active initiatives for the development of metallic membranes for hydrogen separation.

Recently, high permeation rates and separation coefficients were reported using multi-layer ceramic membranes with multi-pore structure controlled at a size ranging from one to several hundred subnanometers. Expectations are high for their use as high-temperature hydrogen separation membranes to supersede conventional porous membrane capacities. The contest between inorganic porous membranes and metallic non-porous membranes is expected to continue.

2.2 Hydrogen storage materials

The storage media for hydrogen are summarized in figure 4.2.1. Compressed gas and liquid hydrogen are hydrogen itself stored in the form of a gas or a liquid, respectively. High-pres-
sure, low-temperature tanks for these are being developed so that they can be built into fuel-cell-powered cars. In this section, we will take a brief look at materials for hydrogen storage inside solids, on solid surfaces or in liquid form, other than in the form compressed gas and liquid hydrogen. Details on development trends are in accordance with recent review articles 4, 5.

Alloys

Hydrogen storage alloys make use of thermodynamic equilibrium whereby a metal absorbs hydrogen at a certain temperature, showing a constant pressure during coexistence of metallic hydride. There was a great progress in hydrogen storage alloys in the 1990s; a BCC alloy has been developed with an effective absorption capacity of around 2.5 mass % at 100 °C.

Inorganic materials

Alanates-based, amidomides-based and borohydrides-based materials are examples of inorganic hydrogen storage materials. Their hydrogen emission temperatures are high and their reaction speeds are low; they are reactive to water and air, making them difficult to handle.

A project aimed at developing materials for storing hydrogen inside solids by going back to basics and incorporating computational chemistry and cutting-edge analysis, Advanced Fundamental Research on Hydrogen Storage Materials 6, was launched by NEDO in 2007 as a five-year plan.

Organic liquid

Cyclohexane-benzene-based and decalin-naphthalene-based materials have been the subject of study for many years as organic liquid hydrogen storage materials because they have a hydrogen content of more than 7 mass % and allow hydrogen emission at 300 to 500 °C.

Metal-organic framework

This group of materials called Metal-Organic Framework (MOF) is a structure made of Zn complex and other complexes that have several nm-sized pores orderly aligned in 3 dimensions, and was first synthesized by Omar Yaghi et. al. They have attained a high hydrogen storage density of 7.5 mass % and 30 g/L at 6 MPa and 77 K 7.

Adsorbent materials

According to precise measurements on hydrogen adsorption of carbon nanotubes taken by the Southwest Research Institute (SwRI), a special research agency assigned by the US Department of Energy, a single-phase nanotube has been able to recreate an adsorption volume of 3 mass % at 77 K and 2 Mpa. However, low apparent density (around 1 g/cm³ even when pressed) poses a problem which would make it difficult for it to compete with compressed hydrogen or other materials.

Furthermore, just recently, a group from UC Berkeley and the Lawrence Berkeley National Laboratory reported on hydrogen adsorption using a polymer with high-specific surface area 8. There are reports that it achieved 5.3 mass % at 77 K and 5 Mpa 9 and is drawing interest for possibilities of further progress.

3. Issues surrounding materials science

With respect to hydrogen production catalysts, a new guidance principle called valence band control has just been discovered and there are hopes for further progress in this area. The key to development lies in the utilization of materials science techniques such as structural control, which skillfully combines phase equilibrium and surface treatment, as well as microstructure control of alloys.

With regards hydrogen refinement materials, on the other hand, control of nanopore structures is necessary in porous membranes, and control of the interface between the membrane itself and the Pd overlayer is important in metallic non-porous membranes, from a heat-resistance perspective.

Similarly, for hydrogen storage materials, control and design of nanostructures are essential for alloy-based, inorganic-based, metal-organic framework and absorbent materials.

For inorganic and organic liquids which would require recovery outside the container, collection and recovery of hydrogen absorption and emission products is a problem that would need to be addressed. Moreover, with nanotubes and other absorbent materials, since these would necessitate low temperature use, materials development would have to be carried out with a view to storage systems appropriate for the intended purpose.

A common issue is the coordination and integration of differing fields, namely between organic and inorganic and between materials and chemical engineering.

References
3) Toray Research Center: Gas separation and refinement techniques (2007) 126.
6) http://unit.aist.go.jp/energy/hydro-star/index.html
9) F. Svec: Unpublished data
1. Basics of materials

Photocatalyst research began to gather momentum after the publication in 1972 of an article by Honda and Fujishima in the journal *Nature* describing the decomposition of water in a photo-electro-chemical cell with a TiO₂ photoelectrode and Pt counter-electrode (now known as the Honda-Fujishima effect). In principle, as shown in Figure 4.3.1, the electrons in the valence band (VB) are excited into the conduction band (CB) by the energy of light. At this time, the positive holes (h⁺) with a positive charge generated in the valence band have strong oxidizing power, and oxidize water to generate oxygen, or strip the electrons from organic hazardous substances and thereby degrade and render these harmless. On the other hand, it is possible to generate hydrogen from water by the reduction action of negatively charged electrons (e⁻) excited into the conduction band.

However, it is not the case that all semiconductors function as photocatalytic materials. As noted above, the premise is that the photoexcited positive holes and electrons have the appropriate oxidizing and reducing power. In other words, the potential of a semiconductor’s valence band must be more positive than the oxidation potential of the object to be decomposed, and simultaneously, the conductive band must be positioned more to the negative side than its reduction potential. Once these thermodynamic necessary conditions have been cleared, for the photocatalytic reaction to proceed, it is further necessary to pass through a complex process wherein the charge is transferred to the surface in an isolated state, and water or organic matter is oxidized or reduced through the production of a surface-active species. Therefore, the materials that actually function as photocatalysts are extremely limited in number.

2. Research trends

In the 1970s, when titanium oxide photocatalysts were discovered, research on hydrogen production by decomposition of water employing semiconductor photocatalysts was vigorously conducted in every country in the world, combined with the global energy crisis signaled first and foremost by the oil shocks of that time. However, before long researchers ran into the wall of the conversion efficiency of titanium oxide, and research on photocatalysts came to a standstill in the 1980s. Figure 4.3.2 shows the light absorptive properties of titanium oxide and the spectra for sunlight and ordinary indoor artificial illumination light (fluorescent lamp). The question of photocatalysts exhibiting catastrophic activity in the light of which wavelength range depends on the size of the forbidden band (band gap) of the photocatalytic semiconductor. In the case of titanium oxide, the band gap is as much as 3.2 eV, so the wavelength is shorter than 400 nm, and it absorbs only the light of the high-energy ultraviolet region. Since ultraviolet light accounts for only about 4% of sunlight, this means that only a minute amount of sunlight energy can be utilized by titanium oxide. A wide-ranging search for materials other than titanium oxide in order to overcome this state of affairs has been undertaken, but the hurdles to practical use remain high.

On the other hand, from around 1990 researchers began seeking out ways to apply titanium oxide photocatalysts to environment cleanups. In particular, the photoinduced super-hydrophilicity discovered in 1994 holds the potential for practical use in many fields. At present, titanium oxide photocatalysts’ high oxidative degradation function towards organic matter, as well as a self-cleaning function that combines their hydrophilizing function, is being applied to such ends as the deodorizing, antibacterial action and antifouling and antifogging.

Along with the development of uses for photocatalytic techniques, there has been strong pressure for research on high activa-
tion of photocatalytic materials. Research on creation of high-specific surface areas with titanium oxide, creation of porous structures with the same and creation of complexes with it and other adsorbents has been conducted actively, with the aim being the rapid degradation and elimination of various organic hazardous substances under the weak ultraviolet light contained in natural light and illumination devices. In addition, the flow of research in recent years is gradually shifting from morphological control of ultraviolet light responsive titanium oxide photocatalysts to the development of visible light responsive materials that can utilize many kinds of light. This is because the chief component of sunlight and indoor lighting is visible light (Figure 4.3.2).

There are several reports of promising materials for which researchers around the world are vying with one another in research and development of visible light responsive photocatalysts, in anticipation of a large-scale expansion of range of application of and market scale for photocatalysts.\(^1\)\(^2\) In addition, research on sunlight hydrogen production by photocatalysts has attracted renewed concern in recent years owing to the deep worries about inadequate petroleum resources and global warming, and breakthroughs are expected in the near future.\(^1\)\(^2\)

### 3. Applications to the environment and energy

#### 3.1 Hydrogen energy production by decomposition of water

While the conductive band electrons reduce water to produce hydrogen, the positive holes of the valence band oxidize water to produce oxygen. This reaction, which is exemplified by the artificial photosynthesis technique, can be termed the most direct and clean method for hydrogen production. If this hydrogen producing technique can be put into practical application, a path may be opened for the fundamental resolution of the problems of scarce supply of petroleum fuel or global warming.

#### 3.2 Degradation and elimination of organic hazardous substances

Environmentally friendly cleanup techniques that utilize only light and eliminate air and water pollution without using energy like electricity, or that exhibit anti-fouling and anti-bacterial action, can be applied ever more widely. The market scale in Japan is reportedly 100 billion yen at present, but it is anticipated that it will reach a market of one trillion yen within a few years.

#### 3.3 Other

The prospects for mitigation of the heat island phenomenon utilizing the photoexcited super-hydrophilicity and for photo-reduction and recycling of carbon dioxide utilizing photocatalysts are being examined.

### 4. Issues in materials science

Since titanium oxide is the only material currently being used in practice, the application of photocatalytic techniques is limited to outdoors or under the presence of ultraviolet light lamps. Therefore, the most important materials science issues related to photocatalysts for supporting the development of photocatalytic techniques is undoubtedly the development and practical application of visible light responsive photocatalysts, which is deemed necessary for an expansion of their use. In addition, basic research on the elucidation of the reaction mechanism, high functionalization, stabilization and so on is also indispensable:

1) There is an urgent need to develop new photocatalytic materials that respond to visible light by band structure control. The establishment of design guidelines by tie-ups with computational science is a pressing matter.

2) High functionalization of photocatalytic materials using nanotechnology is anticipated. In particular, the creation of high-specific surface areas by particle size control, spatial isolation of oxidation-reduction reaction loci by surface nanostructure control, control of surface adsorbent properties, and the imparting of selectivity in photocatalytic reactions by organic-inorganic hybridization or the structure of porous photocatalysts are expected.

3) Many things remain unclear as regards the specifics of the mechanism of photocatalytic reactions. In particular, an elucidation of the behavior of photoexcited carriers, the dynamic behavior of radical species, the behavior of the intermediates produced by these reactions and the degradation behavior of organic compounds are necessary.

4) In order to raise further the practical utility of photocatalytic materials, the preparation of ultrafine catalysts that maintain higher activity and longer operating life and are well matched to the substrate, membrane-formation techniques, and the development of foundation and intermediate layer techniques are all necessary.

5) The development of new functions and uses is being explored.

### References


To those who would like to learn more about photocatalytic materials:

1) Akira Fujishima, Kazuhito Hashimoto and Toshiya Watanabe, Mechanism of Photocatalysts, Nippon Jitsugyo Publishing.
4.4 Fuel Cell Materials

1. Basic knowledge about fuel cells

Fuel cells that utilize the reverse reaction of electrolysis of water to produce electricity from hydrogen and oxygen are anticipated as the trump card among measures for fighting global warming, given that they emit almost no carbon gas and can be expected to generate power with high efficiency.

The development of the six kinds of fuel cells shown in Table 4.4.1 has been promoted based on the difference in the fuel cells’ operating temperature and conduction type among solid electrolytes.

Figure 4.4.1 shows one example of a configuration diagram of a fuel cell. As shown in this diagram, the fuel cell is composed of solid electrolytes and electrodes (anode and cathode), and the design of solid electrolytes exhibiting high performance in the operating environment, and the design of electrode materials exhibiting high performance on the solid electrolytes, become necessary.

Table 4.4.1 Typical features of each type of fuel cell. [1-3]

<table>
<thead>
<tr>
<th>Fuel cell type</th>
<th>Mobile ion</th>
<th>Operating temperature</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline (APFC)</td>
<td>OH⁻</td>
<td>50-200°C</td>
<td>Vehicles and mobile applications,</td>
</tr>
<tr>
<td>Proton exchange membrane (PEMFC)</td>
<td>H⁺</td>
<td>30-100°C</td>
<td>For portable electronic system of low power,</td>
</tr>
<tr>
<td>Direct methanol (DMFC)</td>
<td>H⁺</td>
<td>20-90</td>
<td>200KW CHP systems in use,</td>
</tr>
<tr>
<td>Phosphoric acid (PAFC)</td>
<td>H⁺</td>
<td>~220</td>
<td>All sizes of CHP, 2kW – multi-MW,</td>
</tr>
<tr>
<td>Molten carbonate (MCFC)</td>
<td>CO₂⁻</td>
<td>~650</td>
<td>For medium - of large-scale CHP,</td>
</tr>
<tr>
<td>Solid oxide (SOFC)</td>
<td>O²⁻</td>
<td>All sizes of CHP, 2kW – multi-MW,</td>
<td></td>
</tr>
</tbody>
</table>

In the development of solid electrolytes, mainly the development of oxide-ion conductors and proton conductors has been undertaken actively, but in both these cases the key point is how to be able to construct a path wherein the oxide-ion or proton diffuses at high speed inside materials like oxides or polymers.

In the development of electrode materials, Ni-ZrO₂ is employed for oxide-ion conductors as the anode based on the operating temperature of these conductors, and perovskite-based compounds like LaSrMnO₃ have been examined as cathodes, but the key point of development is how to be able to lower the loss due to overpotential, and at the same time the design of an interface structure formed on the solid electrolyte and electrode interface and the assurance of the stability thereof are reportedly crucial issues.

2. Research trends

Of the various fuel cells noted in Table 4.4.1, this section mainly summarizes the research trends for solid oxide fuel cells and polymer electrolyte fuel cells.

The solid oxide fuel cells (SOFC) that have been developed to date are mainly used in industry as a dispersed power system having several hundred kW.

Currently, concern is focused on the question of how to maximize the performance and stability of such fuel cells at a temperature of about 700-900 °C. Yttria stabilized zirconia and scandia stabilized zirconia are known as representative examples of oxide solid electrolytes, but it is also known that a structure in which the oxygen vacancies called large microdomains are ordered appears in these materials after the long-term stability is assessed. Why is it that such factors causing the conductive properties to decline manifest themselves in zirconia at high temperatures of 700 °C. and above? What can be done to minimize such factors? In order to clarify these questions, the design and development of materials whose conductivity rate does not decline at all and whose stability and reliability are high even in long-term operation of 50,000 hours or 100,000 hours are required. In addition, this is exactly the same in doped ceria, whose potential has been examined in the medium temperature region (300-500 °C.), and there has been a strong wish for basic research and theory building in materials science for such issues common to both zirconia and ceria.

In addition, efforts have also been made to draw out to the maximum extent the electrode reaction activity, and this suggests the possibility that a large uneven stress generated in an electrode substance is exerting an effect on the performance that
the electrode originally has when an electrode is formed on solid electrolytes. There are hopes for the provision of detailed analysis of the nanostructure in such electrode materials, stress analysis based on these analytical results and a basic theory that clarifies the causal relationship of these with the electrode reaction, which is the macro property from such a nanostructure, in the fields of electrode design and defect chemistry in the future.

In the development of polymer electrolyte fuel cells, the development of fuel cells utilizing a Nafion membrane has been mainly conducted to date, but it has been pointed out that there are problems with their stability and performance. Recently research on non-humidified polymer solid electrolytes that operate at temperature of 100 °C and above have attracted attention.

Moreover, research and development is being actively conducted about a large-scale reduction of the amount of rare metals used, such as the platinum or platinum component or ruthenium component in platinum-ruthenium that have been employed as an electrode of such fuel cells, or non-platinum electrodes that do not cause the performance to fall, and hopes have been placed in future advances in research.

“Nanoionics research” can be cited as one part of the activities for probing the prospects for such new materials for fuel cells. It is difficult to provide an account of its specifics in the limited space provided here, so I would like to refer interested readers to the literature cited in the references.

3. Application to environment and energy

Development of a power/hydrogen co-production system

Power/hydrogen co-production system design can be cited as an example that aims at maximum of power generation efficiency by design of a system that integrates hydrogen production and power generation, and tackles the challenge of major technological innovation on the energy and environmental fronts. In this case, the fuel cells are limited to SOFC, and it has attracted a high level of interest as a system exhibiting epochal performance unknown to date. I have major hopes for future advances in this field.

4. Challenges in materials science

The research and development of fuel cells boast a long history, and their origins can be traced back 200 years to “the invention of the principles of the fuel cell by Lord Davy in England in 1801” (from the materials of the Japan Gas Association). In the years since then, the development of fuel cells has witnessed remarkable progress, but they have still not reached the point where they are part of the fabric of our daily lives.

Innovations via the basic research on materials indicated below are needed in order for fuel cells to play the role of a trump card as a measure for fighting global warming as mentioned above.

1) Detailed analysis of the true organization and structure in solid electrolytes and electrode materials made for fuel cells, and materials research and development based on these analytical results.
2) Theoretical analysis of the effects that the nanostructure in the materials exerts on the long-term performance and stability of fuel cell materials.
3) Research and development that integrate three things, nanostructure analysis, simulation and processing.

References
2) Satoru Yanabu and Hisao Nishikawa, Energy Conversion Engineering, Tokyo Denki University Publishing Co.
7) http://www.iis.u-tokyo.ac.jp/cgi/teacher.cgi?prof_id=tsutsu-mi&eng= (see the home page of Professor Tsutsumi, Institute of Industrial Science, Tokyo University).

For those who would like to learn more about photocatalytic materials:
4.5 Secondary Cell Materials

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1. Basics of materials

There are many kinds of secondary battery systems, first among which are lead storage cells, which have long been used, and then nickel-cadmium cells, nickel metal-hydride cells, lithium ion cells, etc. (Figure 4.5.1). Not long ago, a pattern emerged where nickel metal-hydride cells were used for purposes requiring **high power** and lithium ion cells were used for purposes requiring small size and light weight with **high energy density**, such as cellular telephones, but at present lithium ion cells are being used for such ends as power tools. In addition, even though one sees a division into “fuel cells”, “lithium cells” and “other cells” in the pages of the Journal of Power Sources, the representative international journal about chemical cells, it probably suffices at the present point in time to provide an account of secondary cells by restricting myself to lithium cells.

The term “lithium cell” originally referred to cells that employed the metal lithium for the **negative electrode**. Subsequently carbon materials such as graphite were introduced in the negative electrode as a technique for making the cell rechargeable, and when this was further coupled with the adoption of an LiCoO2 positive electrode for achieving **high energy density**, the current lithium ion cell was born.

![Fig. 4.5.1 Energy Density of Various Secondary Cells](image)

2. Research trends

Much of the research to date relating to raising the performance of lithium cells has aimed at an increase in the energy density and a lowering of costs. Since positive electrode materials are high voltage and light weight, their being an oxide of a 3d transition metal has been more or less a necessary condition, and not much room is left for higher energy density. As a consequence, research has focused on lowering of costs, and research on oxides where rare and expensive cobalt is replaced by nickel or cadmium has been conducted. Recently the item that has attracted the most attention is LiFePO4, which uses iron as the **redox element**, which is inexpensive, has extremely low toxicity, and is abundant as a resource. Given that this substance is probably a localized electron system whose electron conductivity is poor, the electrode reaction proceeds in a 2-phase coexistent state, so researchers had concluded that it cannot serve as an electrode that has practical power density. However, data that completely overturns this accepted notion has recently been obtained, and moreover given that it is superior in thermal stability and extremely effective in improving the stability of lithium ion cells, it is being used more widely at present for high power purposes such as power tools and electric automobiles.

Given that no measures for a quantum leap in high energy density can be found for positive electrode materials, hopes have rested on negative electrodes. The representative material thereof is an alloy negative electrode, and the item that is the ultimate target is metal lithium. These materials have high capacity density, and promise higher energy density for cells, but in the former case there is the problem of the cycle life, while in the latter case issues like ensuring safety have not been resolved yet. However, hopes for higher energy density have increased in recent years, and at the same time research on these materials has been reignited, and it is possible to expect major advances as materials science progresses.

In addition to high energy density, high power density can be cited as one of the performance indices sought for cells. However, in general there is a tradeoff between energy density and power density. To put the matter differently, if a materials system having high energy density is developed, it will be possible to achieve higher power by adopting a cell design that lowers the energy density. Owing to this, research on higher power has emphasized cell design rather than basic researches on materials properties, and one example of this is the nanoparticles featuring high power that are being actively researched recently.

3. Applications to the environment and Energy

3.1 Power for automobiles

The proportion represented by energy conversion (power generation) relative to total CO2 emissions in Japan is 30%, and the proportion of the transport sector reaches as much as 20%. Energy conservation is naturally being sought in these fields, and in addition the diversification of energy sources has become an urgent matter as energy restrictions become more stringent in the
transport sector, where Japan’s dependence on petroleum is almost 100%.

With a view to solving these problems, it is anticipated that in the future competition will intensify between various technologies such as fuel cell automobiles, clean diesel automobiles, hybrid automobiles, electric automobiles and substitute fuel automobiles. Of these, secondary cells occupy a key position as the technology common to fuel cell automobiles, hybrid automobiles and electric automobiles.

3.2 Power source for power storage

Various roles are anticipated for secondary cells in the power field as well. Secondary cells are employed as the power source for load leveling, and if it is possible to store the power generated in times bands with low power demand such as nighttime and non-working days and use this power in times bands with large power demand, the fluctuations in the power load can be held in check. As a result, it is possible to reduce the cost of having the power system respond to peak power, and in addition this makes it possible to raise the ratio of atomic power generation or hydroelectric power generation whose CO₂ emissions are low.

In addition, utilization of renewable energy such as solar or wind power is indispensable for solving environmental problems. However, it is impossible to control artificially the amount of energy generated from these sources, since they are affected by the weather and the like. In addition, the power generation sites are usually regions with weak power systems that are located far from the consumption sites in the case of wind power generation, so power transmission becomes a problem. Also, in the case of solar power generation, there is a time-related gap between the amount of power generated and the amount consumed owing to the fact that the people who consume the energy are not at home during the daytime when the power is being generated on the roofs of their homes. In order to solve such problems, and to continue promoting the introduction of renewable energy, it is essential to continue to smooth the linkages of power systems, and the appearance of high performance, low cost secondary cells has been anticipated as something that will contribute to this.

4. Challenges in materials science

In the applications to the environment and energy, it is indispensable to increase the size of the cell, whether one is talking about the cells for electric automobiles or the cells for power storage systems. However, there is a major obstacle to be overcome to achieve this end. This is the problem of safety.

The point on which lithium cells differ from other cell systems is that they generate a high electromotive force in excess of 3 V. Since this voltage vastly exceeds the theoretical decomposition voltage of water, it is not possible to employ aqueous electrolytes with lithium cells as in the case of other secondary cells, and this means that organic solvents are employed instead. Although there have recently been a number of reports about accidents involving lithium cells, the principal cause thereof lies in the fact that this organic solvent is flammable. When the size of the cell increases, not only does the amount of this organic solvent increase, but also heat radiation becomes difficult and the cell temperature rises easily, so the issue of safety becomes more serious. Owing to this, the development of nonflammable electrolytes and the development of electrodes that do not easily reach thermorunaway have become crucial technologies.

In addition, in the transport sector, it is the realization of environment-friendly plug in hybrids, and moreover of electrical automobiles, that is anticipated rather than current hybrids, whose cells are charged only by an internal combustion engine. Even if it is a cell system in which the lithium cells have high energy density, it is said that an energy density that is 7 times what is available at present will be needed for them to substitute for an internal combustion engine. Moreover, when it comes to costs, a cost reduction of 1/40 is required for lithium cells for electrical automobile uses, and an even greater reduction is needed for their spread in the power sector, and revolutionary materials technologies are being sought in order to solve these problems.

References
1. Corrosion resistance of materials

Corrosion progresses due to the same electrochemical reactions as electric cells. Its extent depends on the oxidizing nature of the environment, and the electrode potential is its index. The acidity (pH) is one more representative item serving as an index of the environment, and a phase diagram (potential-pH diagram) that takes these two indices as the two axes is employed as the means for determining the corrosion resistance of metal materials. Figure 4.6.1(a) is a potential-pH diagram of iron (Fe). It is determined that the given metal corrodes if it is in the stable region of ionic species, and this metal does not corrode if it is in the stable region of the metal itself or a substance thereof (an oxide or hydroxide). The oxides or hydroxides of many metals are stable and have corrosion resistance in a specified pH range. However, only Fe has a corrosive region over the full pH range. Such skillful use of Fe can be acknowledged as the place for a researcher in the materials field to show his skill. Even in the case of Fe, though, if the oxidizing nature of the environment is high, the potential enters the stable range of Fe₂O₃, and a thin (nanometer order) and delicate film is produced, and this exhibits corrosion resistance. It is well known that the iron nails placed in concentrated nitric acid exhibit corrosion resistance. Such a state where the metal surface is covered with a thin film is called passivity. Titanium (Ti), nickel (Ni), chromium (Cr), etc. also display corrosion resistance as passive metals. On the other hand, when Cr is added to Fe, the passive region of Cr (Figure 4.6.1 (b)) overlaps on the corrosive region of Fe, and ends up becoming passive and having corrosion resistance as long as it does not become considerably low pH, and such a Fe-Cr alloy is stainless steel. The critical value at which it can no longer be rendered passive is called, pHₐ (Figure 4.6.2), and is the index showing the corrosion resistance of stainless steel, and it is not possible to use this stainless steel in an environment with a pH lower than the critical value. When a chloride ion (Cl⁻) is present even in an environment where stainless steel has corrosion resistance, localized corrosion like pitting or crevice corrosion – the corrosion that occurs under the crevice structure – occurs, and these serve as the initiation site of stress corrosion cracking (SCC). The value of pHₐ also serves as an index of resistance to localized corrosion.

2. Research trends

2.1 Stainless steel

Austenitic stainless steel

Since austenitic stainless steel is superior in corrosion resistance and ease of processing, and retains its toughness even at extremely low temperatures, it can be used for a wide range of purposes. However, its most important drawback is that it causes SCC to occur with the corrosion part as the initiation site in a chloride environment. For example, the upper critical temperature $T_c$ that does not cause SCC is $T_c = 50 \degree C$ in the case of type 304 steel (18 Cr-8 Ni), which is widely used as austenitic general purpose stainless steel, and attempts are being made to raise the $T_c$ to 100 °C and above with a composition that is close to this kind of steel.

On the other hand, one more of the drawbacks of austenitic stainless steel is that it contains Ni, which is a problem due to metal allergies. Even more than the corrosion resistance, Ni is added in order to make the steel into an austenite single phase. High nitrogen austenitic stainless steel, which is set as an austenite phase by adding nitrogen (N) instead of Ni, is being
examined. 4)  

Ferritic stainless steel  
Ferritic stainless steel has the characteristics that it does not include Ni, which is a problem due to metal allergies, and tends not to cause stress corrosion cracking, and so on. However, intergranular corrosion tends to occur easily, and pitting corrosion resistance also declines, due to the carbon (C) and N contained as impurities in the steel. In the past, it was not possible to reduce both of these impurity elements sufficiently, and it has been thought that the corrosion resistance of ferritic stainless steel is inferior to that of austenitic stainless steel. From around 1970, the refining technology for stainless steel improved by leaps and bounds, and it became easy to mass produce steel materials with remarkably low amount of C + N (known as “high purity steel”), and the development of high purity ferritic stainless steel with excellent corrosion resistance was actively pursued. 5) The corrosion resistance of ferritic stainless steel is chiefly determined by the amount of Cr and the amount of molybdenum (Mo), and it is thought that the addition of Ni is effective in improving the mechanical properties, and particularly the toughness. However, Ni addition of 2% and above causes the SCC resistance to decline, so a composition with a good balance of Cr, Ni and Mo is being examined.

2.2 Ni base Alloy  
Ni exhibits good corrosion resistance towards alkali and non-oxidizing acid, and not only has excellent corrosion resistance such as its passivity in a neutral natural environment, but also is superior in its ease of processing and mechanical properties. In addition, alloys that are superior in their chloride stress corrosion cracking resistance are also being developed by making alloys with Cr and Mo. 2) Since these alloys are superior in corrosion resistance, they are used in harsher environments like chemical plants. Owing to this, information about what kind of environment (temperature, Cl⁻ concentration and electrode potential, etc.) it is where these can be used without causing corrosion, in other words the usable range, 1), 2) is also important.

2.3 Titanium  
Ti has superior corrosion resistance owing to the passive film that is formed on the surface. Although it is known that it causes crevice corrosion or SCC in the presence of Cl⁻, alloys with excellent corrosion resistance even in a chloride environment such as Ti-0.15 Pd are being developed. However, since Ti forms a hydroxide due to hydrogen absorption, and this itself is brittle, it exhibits embrittlement as a material (hydrogen embrittlement), so elucidation of the invasive behavior of hydrogen or hydride-forming behavior is awaited. 2)  

3. Challenges in materials science  
The addition of Ni and Mo is effective in improving corrosion resistance. However, the large increase in the price of both metals has become a problem, and metal allergies are an additional problem in the case of Ni. It has become necessary to examine methods for reducing even a little bit the amount of these elements that is added, or replacing them with some other elements. On the other hand, if this is viewed from the standpoint of the user of the materials, it is said that type 304 steel causes SCC at temperatures of 50 °C and above, but in reality there are also cases where SCC does not occur in type 304 steel in a Cl⁻ environment of 50 °C and above, and it is necessary not only to elucidate the mechanism of these forms of corrosion but also to clarify “when, where and how” it occurs and continues to grow.

References  
Chapter 5. Materials for High-Efficiency Major Power Plants

5.1 Overview

Fujio Abe
Heat Resistant Design Group, National Institute for Materials Science

1. Japan’s power generation and CO₂ emissions

Ever since Japan experienced its second oil shock in the 1970’s, oil-fueled thermal power plants have continually decreased (Figure 5.1.1). Instead, power plants using nuclear power, natural gas, or coal have increased, and in 2003 were responsible for 80% of total power generation, becoming the major among power generation options.

The amount of CO₂ that a power station emits per unit of generated power (the unit CO₂ emission) is greatest for coal, due to the fraction of the fuel that is consumed, and oil and natural gas are a little less but still large compared to other types (Figure 5.1.2). Therefore it is necessary to increase efficiency by using steam or gas under high temperature and high pressure to turn turbines in order to reduce CO₂ emissions. The CO₂ emissions from nuclear power stations are low, but it is necessary to increase their efficiency through higher temperatures by pursuing technological developments, such as with fast breeder reactors that can make more efficient use of uranium than the light water reactors currently in use, or with fusion reactors that do not use uranium but whose radioactive waste must be greatly reduced.

2. Material issues related to higher efficiency: Grain boundaries, interface stability

Among high-temperature structural materials for nuclear power, natural gas, and coal (Table 5.1.1), ferritic steel is less expensive than either austenitic steel or Ni-base superalloys and has the advantage of less thermal stress because it has lower thermal expansion and higher thermal conductivity, but its high-temperature creep strength is low because of its high diffusion rate.

Research to expand the usable critical temperature of various materials by increasing the high-temperature creep strength has focused mainly on the grain boundaries and the interface between the second phase and the matrix, and on improving the long-term stability of fine precipitates at elevated temperature (Figure 5.1.3). Also, the key issues in the thermal power are to clarify the mechanisms on high-temperature oxidation, high-temperature corrosion, and coating film characteristics, while in the field of nuclear power, the key is to clarify the mechanism by which irradiation damage due to high-energy neutrons and atoms (H, He) that are created by nuclear transmutation reactions affect the dislocation dynamics and phase stability.

Table 5.1.1 Examples of next generation high-temperature structural materials for major power plants

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Target Temperature</th>
<th>Applications</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferritic steel</td>
<td>650 °C</td>
<td>A-USC main steam pipes, FBR piping</td>
<td>Martensitic microstructure</td>
</tr>
<tr>
<td>Austenitic steel</td>
<td>700 °C</td>
<td>FBR core, fast breeder blanket for fusion reactor</td>
<td>Subcritical embrittlement</td>
</tr>
<tr>
<td>Ni-base superalloys</td>
<td>750 to 770 °C</td>
<td>A-USC steam turbine main steam pipe</td>
<td>Target single crystal alloy</td>
</tr>
<tr>
<td></td>
<td>1,500 °C</td>
<td>Combined cycle gas turbine blades</td>
<td>Single crystal alloy</td>
</tr>
</tbody>
</table>

Fig. 5.1.1 History of power generation in Japan

Fig. 5.1.2 CO₂ Emission per unit of generated power

Fig. 5.1.3 (a) γ/γ’ interfaces in a Ni-base single crystal alloy, (b) VN nano-precipitates at boundaries in a 9% Cr ferritic steel

3. Keywords from materials science

<table>
<thead>
<tr>
<th>Items</th>
<th>Keywords</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) High-temperature mechanical properties</td>
<td>Yield stress, tensile strength, creep strength (lifetime), fatigue strength, creep-fatigue interaction, ductility, toughness</td>
</tr>
<tr>
<td>2) Phase stability</td>
<td>Crystal grain, subgrain, grain boundary, subgrain boundary, diffusion, precipitation, phase transformation, lattice defect (point defect, dislocation, interface), oxidation-corrosion, irradiation defect</td>
</tr>
</tbody>
</table>

References

To reduce CO₂ and curb global warming while saving energy, it is necessary to have great improvements in the efficiency of gas turbines, such as by using \textit{liquid natural gas driven combined-cycle power generation}, thereby achieving a great reduction in CO₂ as coal-firing thermal power stations are replaced by them. In the “Cool Earth 50” concept of cutting in half the CO₂ emission that causes global warming by the year 2050\(^1\), and in the 21 revolutionary technologies chosen by the Agency for Natural Resources and Energy in order to realize that goal\(^2\), leading-edge gas turbine power generating technology is indicated as a revolutionary technology of high priority, and it is expected that planning will be accelerated as we move toward the 2008 Toyako summit.

The most effective way to increase the efficiency of a thermal engine is to raise the turbine inlet temperature, which represents the maximum temperature of the Carnot cycle, and there are activities both within Japan and abroad to develop the materials required to achieve this goal, especially with regard to the Ni-base superalloys that are used in turbine blades. Table 5.2.1 shows the Ni-base superalloys for turbine blades that are used in the gas turbines of the newest natural gas combined-cycle power generation\(^3\), and Table 5.2.2 shows the compositions of representative Ni-base single-crystal superalloys.

Figure 5.2.1 shows the history of thermal efficiency improvements for different types of thermal power generation. Natural gas combined-cycle power generation has reached a thermal efficiency of 52%, making them the most efficient type of thermal power generation at present. As part of the \textit{High Temperature Materials 21 Project}\(^4\), the basic research required to further increase the inlet gas temperature from the current value of 1500

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### Table 5.2.1 Ni-Base Superalloys Used in Turbine Blades of the Latest Liquid Natural Gas Driven Combined-Cycle Power Generation

<table>
<thead>
<tr>
<th>GE-HTacch-Tohoku</th>
<th>GE-Tohoku</th>
<th>MIE</th>
<th>FG-Siemens</th>
<th>KHI-Abton</th>
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</thead>
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<tr>
<td>Composition</td>
<td>Substrate</td>
<td>Cooling</td>
<td>Substrate</td>
<td>Cooling</td>
</tr>
<tr>
<td>GE-HTacch-Tohoku</td>
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<td>TBC</td>
<td>GTD-111</td>
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<tr>
<td>GE-Tohoku</td>
<td>GTD-111</td>
<td>Air</td>
<td>Mo/Nb</td>
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<td>MIE</td>
<td>GTD-111</td>
<td>Air</td>
<td>Mo/Nb</td>
<td>GTD-111</td>
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<tr>
<td>FG-Siemens</td>
<td>GTD-111</td>
<td>Air</td>
<td>Mo/Nb</td>
<td>GTD-111</td>
</tr>
<tr>
<td>KHI-Abton</td>
<td>GTD-111</td>
<td>Air</td>
<td>Mo/Nb</td>
<td>GTD-111</td>
</tr>
</tbody>
</table>

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### Table 5.2.2 Compositions of Ni-Base Single-Crystal Superalloys Used in Turbine Blades (wt%, remaining Ni)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Al</th>
<th>Ti</th>
<th>Nb</th>
<th>Ta</th>
<th>Hf</th>
<th>Re</th>
<th>B</th>
<th>Zr</th>
<th>Others</th>
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<td>PWA1480</td>
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<td>10</td>
<td>4</td>
<td>5</td>
<td>1.5</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>CMSX-2</td>
<td>4.6</td>
<td>6</td>
<td>0.6</td>
<td>8</td>
<td>5.5</td>
<td>-</td>
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<td>-</td>
<td>1(^e)</td>
</tr>
<tr>
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<td>10.9</td>
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<td>-</td>
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<td>1(^e)</td>
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<td>9</td>
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<td>3</td>
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<tr>
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<td>8</td>
<td>7</td>
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<td>6.5</td>
<td>0.1</td>
<td>3</td>
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<td>-</td>
<td>-</td>
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<td>YH 61</td>
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<td>8.9</td>
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<td>1.4</td>
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<td>6</td>
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<td>5.9</td>
<td>-</td>
<td>5.6</td>
<td>0.1</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>TMS-162</td>
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<td>3.9</td>
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<td>5.6</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>6 Ru(^d)</td>
<td></td>
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<tr>
<td>TMS-196</td>
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<td>2.4</td>
<td>5</td>
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<td>-</td>
<td>5.6</td>
<td>0.1</td>
<td>6.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5 Ru(^d)</td>
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</tbody>
</table>
°C to as much as 1700 °C, and to increase thermal efficiency from 52% to the range of 56% to 60% (HHV base), has been underway since 2004 in various joint efforts, such as those between the Ministry of Education, Culture, Sports, Science, and Technology and the National Institute of Materials Science, and between the Agency for Natural Resources and Mitsubishi Heavy Industries. By replacing half of the previous conventional thermal power stations, such as those that are coal-firing, with ones that have a thermal efficiency of 56%, it is calculated that the total CO₂ emissions within Japan can be reduced by 4%, and the key to realizing this is high temperature technology, such as for turbine rotor blades. Ni-base superalloy turbine blades usually have a thermal barrier coating (TBC), and they control the metal temperature from the inside with air cooling or steam cooling so that they can be used within a gas flow having a temperature higher than their melting points. However, the cooling process is itself a factor that reduces the thermal efficiency, so there is a need for alloys to withstand as high temperature as possible in order to minimize the required cooling.

Ni-base superalloys have evolved from forged alloys to the conventionally cast alloys, directionally solidified alloys, and single-crystal alloys. At present, single-crystal superalloys are being used for first-stage turbine rotor blades. Figure 5.2.2 shows the temperature capabilities for representative single-crystal superalloys in each generation, from the first to the fifth generation. At the present time alloys up to the second generation are widely used in gas turbines for power generation. The High Temperature Materials 21 Project, using the fifth generation single-crystal superalloy TMS-196, is the first in the world to succeed in the casting of single-crystal turbine blades as large as 30 cm in length.

Increasing the temperature of turbine blades has also become an important issue for the small turbines used for cogeneration (supplying both heat and electricity) in order to increase power generating efficiency and to improve the electricity to heat ratio. As shown in Figure 5.2.3, it is expected that these gas turbine technologies will have repercussions in various fields, such as with coal gasification combined-cycle power generation for which a pilot plant is currently in operation at Nakoso, and with the smaller, safer, high-temperature gas reactors (helium turbines) whose introduction is being tested in places such as South Africa. A future issue for the development of these alloys is whether it will be possible to develop advanced alloys at lower cost in order to address the rising prices of metal resources.

Active research is under way both within Japan and abroad in the development of very high temperature materials for raising the temperatures and efficiencies of airplane engines, which are also a type of gas turbine engine, but this will be introduced in Chapter 6 when airplane engine materials are discussed.

References
4) National Institute for Materials Science, High Temperature Materials Center home page:http://sakimori.nims.go.jp
5.3 Ultra Supercritical Coal-Fired Power Generation Materials

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1. Basics of Materials

Coal-Fired Power Generation, which burns coal in order to drive a turbine with high-temperature high-pressure steam, are one of the main pillars of Japanese power generation because there are abundant underground coal deposits throughout the world, so that there is a cheap and stable price for coal. However, the CO₂ emissions are large, so materials are being developed for ultra supercritical (USC) power generation, which improve power generation efficiency by using high-temperature high-pressure steam while reducing CO₂ emissions. Plants whose steam conditions exceed 566 °C and 24.1 MPa are called USC plants, and the highest steam temperatures at the newest USC plants are about 610 °C. Plants with steam temperatures of 700 °C or more are called A-USC (advanced USC) plants. Projects are currently under way in Japan, America, and Europe to develop materials for A-USC (Figure 5.3.1).

Besides A-USC, another hopeful technology for using coal cleanly and with high efficiency is integrated coal gasification combined-cycle (IGCC) power generation, which gasifies coal and uses it as a fuel. We hope that, for both A-USC and IGCC, their various advantages will be put to appropriate use in the future. The power generation efficiency of A-USC is estimated at 46% for a steam temperature of 700 °C, and 47.5% at the 750 °C level, and this is similar to the efficiency of IGCC at the 1500 °C level1. A high efficiency of 49% is estimated for A-USC at the 800 °C level.

2. Research Directions in Europe and America

In Europe, since 1998, the THERMIE project has been progressing toward its targeted steam conditions of 35.5 MPa/700 °C/750 °C (main steam pressure, main steam temperature, reheat-ed steam temperature). THERMIE consists of three phases: AD700 materials development, COMTES700 component testing, and demonstration testing1. A plant’s steam temperature usually means the temperature of the main steam pipes. Figure 5.3.2 shows a conceptual drawing of a 700 °C class turbine, in which the use of Ni-base superalloys, which have large high-temperature creep strengths but are expensive, is limited only to the highest temperature portions, and inexpensive ferritic steel, whose linear expansion coefficient is small, is used for the next highest temperature portions. Thus it is a welded structure of a Ni-base superalloy and ferritic steel. Austenitic steel is not used for the turbine because its linear expansion coefficient is large.

In the boiler system, for the thin-walled small-diameter tubes of the super heater, austenitic steel that has a creep rupture strength of 100 MPa for 10⁵ hours at 700 °C, and Ni-base superalloys that have a creep rupture strength of 100 MPa for 10⁵ hours at 750 °C, are being developed. For the main steam pipes, there is research to strengthen 9 to 12 Cr ferritic steel and expand its maximum allowable temperature up to 650 °C, and to develop Ni-base superalloys with creep rupture strength of 150 MPa for 10⁵ hours at 700 °C. The Ni-base superalloy research is not looking for new alloys but rather improving and optimizing existing alloys within standardized composition ranges.

In America, the 760 °C class A-USC project “DOE Vision 21”, which began in 2001, is sponsored by the Department of Energy and the Ohio Coal Development Office. Its research and development is being pursued by the Electric Power Research Institute (EPRI), the Oakridge National Laboratories, and the American manufacturers. DOE Vision 21 is not expected to develop new materials, but rather to look for existing high-strength materials from manufacturers in Japan and Europe, and then evaluate them to select candidates.

![Fig. 5.3.1 History of Steam Conditions and A-USC Projects](image)

![Fig. 5.3.2 Conceptual Drawing of Europe’s 700 °C Class Turbine](image)
3. Research Directions in Japan

The 700 °C class A-USC project, which is considered economically significant, will begin in 2008. In addition to the development of 700 °C class Ni-base superalloys and austenitic steel, and 650 °C class ferritic steel, this will also include conceptual design, economic evaluation, and materials standardization. In order to limit the use of expensive Ni-base superalloys as much as possible, the plan is to expand the maximum allowable temperatures of ferritic steel and austenitic steel and apply a dissimilar metal welded construction, while designing an efficient cooling structure for the turbine.

Even before the start of this project, the materials development was partially being done by private companies. In addition to using γ' to provide additional strength, private companies developed Ni-base superalloys with small linear expansion coefficients (LTES700, USC141, TOS1X) and Ni-base superalloys that are excellent for manufacturing with large ingots (FENIX700). LTES700 has a smaller linear expansion coefficient than that of austenitic steel or other Ni-base superalloys used for A-USC (Alloy 617, 625, 706) (Figure 5.3.3).

In addition to Ni-base superalloys, high-strength austenitic steel (HR6W) has also been suggested as a candidate material for 700 °C class main steam pipes in boiler systems, and there are development efforts aimed at increasing the creep strength for 10^5 hours at 700 °C to 100 MPa, and at developing production technique for large-diameter thick-walled pipes. Developments in ferritic steel are aiming at materials with a stable long-term creep strength that can be used up to 650 °C without any degradation in creep strength in the welding joints compared to the base metal.

Thus, the 9 Cr steel with boron additive, as developed at NIMS, has the advantage that it does not exhibit any degradation in creep strength in welded joints (Figure 5.3.4). Also in dissimilar welded joints with ferritic steel and austenitic steel (and similarly for Ni-base superalloys), at high temperatures of 600 °C or more, the creep strength loss is serious in the heat affected zone of the ferritic steel side due to Type IV creep damage, so it is important to suppress the creep strength loss in the ferritic steel welded joints.

4. Issues for the Future

We need to make clear the long-term behavior of ferritic steel and Ni-base superalloys. The 10^5-hour creep rupture strength of newly developed Ni-base superalloys at 700 °C, as extrapolated from temperature accelerated creep tests, attains the target value of 100 MPa, but the experimental verification by long-term creep tests at 700 °C is desired. Many points also need to be clarified with regard to the long-term creep-fatigue interaction, which is correlated with microstructural stability and ductility.

References

1. Introduction

Nuclear fission of heavy elements like uranium and nuclear fusion of light elements like hydrogen are the two nuclear reactions applicable for the generation of electricity. Thermal energy is produced by these nuclear reactions and utilized to operate a steam turbine for the electrical generator. Nuclear power generation by fission reaction of uranium is already commercialized and now supplies more than 30% of electricity in Japan. Fusion energy, on the other hand, has been regarded as an inexhaustible energy resource that could save the world, and International Thermonuclear Experimental Reactor (ITER) is now being constructed as a big step toward its realization. One of the most essential problems for the fusion/fission power materials is the radiation damage which is a degradation caused by high energy particles like neutrons produced in the nuclear reactions. In this article the radiation damage is briefly explained and the status of research and development of fusion/fission power materials will be described.

2. Radiation Damage

Fig. 5.4.1 shows how the crystal lattice atoms are displaced by incident neutrons. Such atomic displacements produce point defects (interstitial atom and atomic vacancy). Occasionally the displaced atom itself can force other atoms out of their lattice points and this phenomenon is called cascade damage. Most of the point defects would annihilate through mutual recombination or absorption by grain boundaries or dislocations. Portion of point defects, however, agglomerate and continuously grow under irradiation. In general vacancies form three-dimensional void (cavity), resulting in a swelling of materials, and interstitial atoms form two-dimensional dislocation loops, mainly responsible for radiation hardening and conversely an enhanced creep deformation under irradiation. Moreover, point defect reacts with solute atoms in the material so that its migration causes a locally high concentration of solutes, which is called irradiation-induced segregation and affects various properties like corrosion.

Reaction cross-sections for \((n, \alpha)\) and \((n, p)\) increase steeply as neutron energy is higher than about 5 Mev, and resultant nuclear transmutations will produced large amounts of transmuted elements and gases (helium and hydrogen), which is called transmutation damage. Most of the transmuted elements are radioactive and would be a burden to the environment. The produced gaseous atoms may possibly induce embrittlement and degrade the mechanical properties considerably.

3. Fusion Reactor Materials

Figure 5.4.2 schematically shows ITER. ITER is a Tokamak type fusion device, which magnetically confines the fusion plasma of deuterium (D) and tritium (T), and its major mission is to prove a long-lasting burn of D-T fusion plasma. Since neutrons with energy as high as 14 MeV are produced in the D-T fusion plasma, the first-wall/blanket components, which protect a vacuum vessel and superconducting magnets, will be exposed to an extremely severe environment. Thus, these components consist of modules and will be replaced during the ITER operation (20 years)\(^1\). Beryllium will be applied to the plasma-facing portions and copper alloys dispersion-strengthened with alumina will be used for the thermal sinks. Outer portions of the blanket will be made of nitrogen-added low-carbon steel (316LN-ITER grade)
which shows good high-temperature strength.

In DEMO (the next device after ITER, and the first to generate electricity) fusion plasma will be more intense and the first-wall/blacket materials will be exposed to a much harder damage at higher temperatures. Therefore, materials with excellent swelling resistance and thermal conductivity are required for the first-wall/blacket components. In addition low-activation materials composed of specific elements of which radio-activity would decay swiftly after the nuclear transmutation are essential for the sake of environments. All the above consideration leads to low-activation ferritic steels as the most promising structure material, and the synergetic effects of irradiation and externally applied loads (stresses and environments) have been vigorously investigated. Also, vanadium alloys and SiC-composites are expected to be low-activation fusion materials with more excellent high-temperature strength.

4. Fission Reactor Materials

Electric power generation by light water moderated reactors (LWRs) has already been established. Figure 5.4.3 shows the basic components of a pressurized water reactor (PWR). Since the energy of neutrons produced by the fission reaction is about 1 MeV at the most, transmutation damages are not so serious in LWRs. Major materials used are zirconium alloys, which show low neutron absorption and good corrosion resistance, for the fuel cladding, nickel alloys for the steam generator, and SUS 304 and SUS 316L for the in-core structure components. Irradiation-induced stress corrosion cracking (IASCC) induced by the deterioration of corrosion resistance through irradiation-induced solute segregation has been worried about as the reactor aging has been proceeding. For the suppression of IASCC, SUS 316L with lower phosphorous content and austenitic stainless steels with high chromium content have been considered.

The fast breeder reactor (FBR) has been developed as the next-step fission nuclear reactor following LWR. FBR shows utilization efficiency of uranium of about 60%, much higher than that of about 0.5% in LWRs, capable of using the uranium resources far more efficiently. In the demonstration FBR Monju, SUS 304 is used for the reactor vessel and the pinging from the viewpoint of compatibility with liquid sodium coolant, and SUS 321 or 2 1/4Cr-Mo steel is applied to the components in contact with boiling water such as the steam generator. In the development of next-step demonstration FBRs, SUS 316LN steels modified with trace elements such as Ti or Nb and improved 9Cr-1Mo steels have been considered for the reactor vessel and for the steam generator, respectively. Efforts are now being made to gather and expand the database for these advanced FBR materials.
Chapter 6. Materials for Energy Transmission and Conversion

6.1 Overview

This chapter reports on materials concerned with the transportation of energy and objects, and on materials concerned with energy conversion. All these materials can contribute to environmental conservation by saving energy consumption, and are important in practical applications. A variety of materials could serve these purposes. Superconductors and lightweight structural materials are examples of the first type.

“Superconductivity” is the phenomenon by which the electrical resistance of some kinds of electrically conductive materials drops to zero at low temperatures. If superconductivity could be used for transmitting electricity, it would make it possible to carry current without energy loss. Very high currents must be carried for practical application and, therefore, the development of materials such as these is essential.

“Lightweight structural materials” are those which are light yet strong enough for use in transport equipment. The weight of machinery can be reduced by using these high-specific strength materials, reducing the energy required for transportation. This chapter mainly discusses lightweight structural materials for automotive use.

Materials for energy conversion, on the other hand, include magnetic refrigerants, nanocomposite magnets, mechanical response materials, low-friction materials and aircraft engine materials.

“Magnetic refrigeration” exploit a phenomenon by which a magnetic field applied to a magnetic material aligns magnetic moments, then the orientation of the moments becomes random when the field is removed, and the temperature of the material drops. This kind of magnetic refrigeration is more efficient than conventional vapor refrigeration, helping to save energy. Another advantage is that they do not use CFCs or other refrigerants, so they cause very little environmental pollution.

“Permanent magnets” are used in motors and generators, and their efficiencies are improved by increasing the performance of magnets, therefore saving energy. Recently, they have become more remarkable for their use in hybrid cars and fuel cell electric vehicles, and expectations for high-performance magnet development are now rising. Nanocomposite magnets have smaller crystal grains than single-domain magnetic particles, so they deliver better magnetic performance.

“Mechanical response” is the conversion of heat energy (input) to mechanical energy (output). Shape-memory alloys are used to obtain usable mechanical energy from heat sources. Shape memory is the phenomenon in which a material deformed by the application of force returns to its original form when heated.

“Low-friction materials” can reduce the friction in various machineries, saving energy by minimizing the conversion of mechanical energy to heat and other forms of waste energy. Use of lubricants is one way to reduce friction, and the development of high-performance lubricants such as Fullerences, described in this chapter, are a particularly promising example.

“Aircraft engine materials” are important for use in jet engine turbines, where they are exposed to high temperatures. The efficiency of jet engines increases with the increase of combustion temperature, so materials that deliver adequate strength and reliability even at high temperatures are required. In this chapter we will introduce several superalloys with superior strength at high temperatures.

<table>
<thead>
<tr>
<th>Items</th>
<th>Keyword</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Material structure control</td>
<td>Coagulation, alignment, crystal grains, precipitation, phase transformation, aging, recrystallization, epitaxial growth, forging, sintering, martensitic transformation</td>
</tr>
<tr>
<td>2) Electrical characteristics</td>
<td>Electrical resistance, anisotropy, critical current density, weak coupling, insulation</td>
</tr>
<tr>
<td>3) Magnetic characteristics</td>
<td>Anisotropy, magnetic moment, magnetic domain, residual magnetization, coercive force, saturation magnetization, upper critical field</td>
</tr>
<tr>
<td>4) Heat management</td>
<td>Thermal conductivity, specific heat, Carnot cycle, adiabatic demagnetization, magneto-caloric effect, cool storage equipment, coating</td>
</tr>
<tr>
<td>5) Mechanical strength control</td>
<td>Elasticity, superelasticity, plasticity, tensile stress, yield stress, toughness, friction, lubrication, abrasion, shape-memory effect</td>
</tr>
</tbody>
</table>
1. Introduction

Superconductors can carry large currents with zero resistance. When applied to various electrical devices, they not only raise efficiency, they can also reduce the size and weight of the devices, therefore they save energy and help to conserve the global environment. For superconductors to be usable in electrical power applications, they must be formed into wires or tapes. The superconducting materials currently being researched for wire and tape fabrications can be classified into metal-based and oxide-based. The two that are already ready for practical use are Nb-Ti and Nb₃Sn, both metal-based superconductors. Since the discovery of high-temperature oxide superconductors, for which the superconducting transition temperature \( T_c \) is above the temperature of liquid nitrogen (77K), many researchers have been working on forming them into wires and tapes. Recently, it has become possible to form long, high-performance wires and tapes, so discussion of practical applications has begun in earnest. The newly-discovered MgB\(_2\) is a metal-based superconductor. It has a \( T_c \) of approximately 40K, which is very high for the metal-based superconductor. That has prompted intensive research into wire fabrication of MgB\(_2\) \(^1\).

2. Development of superconducting wires and tapes

The high-temperature oxide superconductors with the greatest promise for practical applications are bismuth-based and yttrium-based oxides. High-\( T_c \) oxide superconductors have the problem of weak couplings between crystal grains. To overcome this problem, it is necessary to arrange the crystal grains of such superconductors in the same orientation (alignment). Alignment greatly improves the strength of couplings between crystal grains, allowing the material to carry large superconducting currents. The bismuth-based oxides are Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_x\) (Bi-2212) and Bi\(_2\)Sr\(_2\)Ca\(_2\)Cu\(_3\)O\(_y\) (Bi-2223), and the most common wire fabrication method, which can be applied to both materials, is the Powder-In-Tube (PIT) method, in which powdered raw materials are packed into metal tubes for processing and heat treatment \(^2\) \(^3\). Silver is used for the metal tubes. Figure 6.2.1 shows an example of transverse-section Bi-2212 wire. \(^2\)

Yttrium-based oxide YBa\(_2\)Cu\(_3\)O\(_y\) (Y-123) has less two-dimensionality than bismuth-based oxides, and its critical current density \( J_c \) is much better than Bi-based oxides. However, uniaxial alignment (c axis alignment) is inadequate to achieve high superconducting current between crystal grains, so biaxial alignment is required. Therefore, research is mainly concentrated on forming a coating of Y-123 on a metal substrate tape using the vapor deposition process, producing what are normally called coated conductors \(^4\). The method which currently achieves the longest tape is the IBAD (Ion Beam Assisted Deposition) method. The key point of the method is that it uses an unaligned metal substrate tape of Hastellox etc., and forms a biaxially aligned coating of a buffer layer of Ytria Stabilized Zirconia (YSZ) or similar material. The biaxial Y-123 layer is formed by epitaxial growth on the aligned buffer layer, using the Pulsed Laser Deposition (PLD) method.

MgB\(_2\) has a high \( T_c \) value, but is still free of the weak couplings between crystal grains which affect high-temperature oxide superconductors, so MgB\(_2\) appears to have an advantage in this area. The low cost of the raw materials and the applicability of simple wire fabrication method mean that MgB\(_2\) also has an advantage in cost reduction. Research is now under way to extend the PIT method for wire fabrication to MgB\(_2\) as well \(^5\). The upper critical field \( B_{c2} \) of MgB\(_2\) wire at 20K is nearly 11T, which rivals the B\(_{c2}\) at 4.2K for most widely used Nb-Ti. That suggests that the Nb-Ti wire, which is currently in use at 4.2K, could be replaced with MgB\(_2\) wire, enabling operation at temperatures of ~ 20K, using convenient refrigerators or liquid hydrogen.

With the PIT method, \( J_c \) values exceeding 100kA/cm\(^2\), regarded as the threshold for practical use, are achieved in a 2T magnetic field at 20K, and application in a relatively weak magnetic field is thought to be possible even at the current \( J_c \) level. However, \( J_c \) falls rapidly with increasing magnetic field, declining to 12kA/cm\(^2\) in a 5T magnetic field.


3. Applications of superconducting wires and tapes

Specific applications include power transmission cables, generators, motors, transformers, superconducting magnetic energy stores (SMES), current-limiting devices, magnetic separators and current leads. Intensive work is now being dedicated to the construction of prototypes for such devices. For power transmission cables, cable based on Bi-2223 tape and cooled by liquid nitrogen have been developed and are now tested in many places. In Albany city, New York State, USA, a 350m-long superconducting power transmission cable has been built into and used in the real power grid. It has supplied electric power to 70,000 households for nine months. Figure 6.2.2 shows that power transmission cable. A prototype 30m-long power cable using Y-123 coated conductor will also be built and will be used to replace a portion of the above 350m cable in operation.

Prototypes for superconducting ship motors, superconducting transformers and similar applications have been constructed with Bi-based wires. Bi-based oxide magnets have also been installed in the JR Tokai maglev train and tested. Production is also pressing ahead on prototypes for MRI magnets, generators and other applications for MgB2 wires.

4. Task for the future

The most important challenge is to improve the Jc characteristic for bismuth-based oxide wires. The key to that improvement probably lies in improving orientation and reducing impurities. In general, the production processes for high-Tc wires and tapes are complex, and costs tend to be high, so it is very important to reduce their costs. There are many points that should be studied to that end, such as ways of streamlining wire production processes.

Y-123 coated conductors show high Jc values, but Jc per unit area (Jc) across the whole cross section including substrates and buffer layers is not very high. It is necessary to improve grain alignment by the structure control, and to consider measures such as making the Y-123 layer thicker and stacking of layers. The speed of coating formation is important for cost, and it must be accelerated to raise the speed of tape production.

In MgB2 wires, Jc has not yet reached the level of practical use, and the biggest challenge is to raise it. With MgB2 wire formed by the PIT method, the MgB2 filling factor is rather low, at around 50%, so it should be possible to substantially improve Jc by raising the filling factor. It is also important to reduce the levels of impurities such as MgO.

As described above, control of material structure appears to hold the key of the practical development for each wire and tape material, and long-running researches based on materials science should continue to that end.

Bibliography
6.3 Magnetic Refrigerants

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1. Basics of the material

Magnetic refrigeration makes use of magnetocaloric effect, and is well known as an efficient method in principal because its cooling cycle can most closely follow the Carnot cycle.

The magnetocaloric effect is caused by the entropy change of magnetic moments due to an external magnetic field. As figure 6.3.1 shows, the magnetic moments of a magnetic material placed in a magnetic field attempt to align with the field, reducing the magnetic entropy. At that stage, the material generates heat and its temperature rises. On the other hand, when the magnetic material is removed from the field, the magnetic moments attempt to return to random state, so magnetic entropy rises, causing heat absorption or temperature reduction. Compared to gas compression-expansion methods, pressure can be regarded as analogous to the magnetic field, and volume of gas to the magnetization of the magnetic material.

The magnetic entropy change of a magnetic material with magnetic moment \( J \) is given by \( \ln (2J+1) \). In the gas expansion cycle, changing pressure from \( P_1 \) to \( P_2 \) produces an entropy change of \( \ln \left( \frac{P_2}{P_1} \right) \), so if, for example, a magnetic substance with \( J=7/2 \) is used, then \( \ln (2J+1) = \ln (8) \), which means the refrigeration effect is equal to a gas expansion cycle in which the compression ratio \( P_2/P_1 \) is 8.

Magnetic refrigerants are selected with reference to their magnetic entropy change per unit volume, magnetic transition temperature, lattice entropy, thermal conductivity, chemical stability, electrical insulation, and other properties. Table 6.3.1 shows typical examples of magnetic materials used as magnetic refrigerants.

<table>
<thead>
<tr>
<th>Substance name (abbrev.)</th>
<th>Magnetic transition temperature (K)</th>
<th>Refrigeration cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuK(SO₄)₂·12H₂O = CPA</td>
<td>0.009</td>
<td>Carnot</td>
</tr>
<tr>
<td>Fe₃(Fe₅O₇)₋₁₂H₂O = FAA</td>
<td>0.026</td>
<td>Carnot</td>
</tr>
<tr>
<td>Dy₅Gd₇O₂₁₂ = GGG</td>
<td>0.65</td>
<td>Carnot</td>
</tr>
<tr>
<td>Dy₆Al₅O₁₇ = DAG</td>
<td>2.4</td>
<td>Carnot</td>
</tr>
<tr>
<td>ErAl₂</td>
<td>12</td>
<td>AMR</td>
</tr>
<tr>
<td>GdPd</td>
<td>38</td>
<td>AMR</td>
</tr>
<tr>
<td>DyAl₂</td>
<td>63</td>
<td>AMR</td>
</tr>
<tr>
<td>Gd₅Ni₂</td>
<td>71</td>
<td>AMR</td>
</tr>
<tr>
<td>Gd₅S₂₄₅Ge₃ₓ</td>
<td>120</td>
<td>AMR</td>
</tr>
<tr>
<td>Gd₅Si₂Ge₇</td>
<td>260</td>
<td>AMR</td>
</tr>
<tr>
<td>Gd₁</td>
<td>293</td>
<td>AMR</td>
</tr>
<tr>
<td>La(Fe₃S₁₀)₀₁₋₀₂Hₓ</td>
<td>200–330</td>
<td>AMR</td>
</tr>
</tbody>
</table>

2. Research trends

Magnetic refrigeration was well known as the adiabatic demagnetization refrigeration (ADR) to provide ultra-low temperatures in early 20th century. In the 1980s, Carnot type magnetic refrigeration successfully demonstrated to provide superfluid or liquid helium with extremely high efficiency. Currently, variety of magnetic refrigerators is being developed including ultra-low temperature for space application, hydrogen liquefaction and room-temperature coolers.

Magnetic refrigerator consists of magnetic material, thermal switch and magnet. The thermal switch is used to control the heat flow to/from the magnetic material such in an isothermal or adiabatic state. Typical properties of the thermal switch are; thermal switch ratio (the ratio between thermal conduction values in the on and off states), maximum heat transfer rate, and the time and energy required for switching. Since the magnetic refrigeration cycle needs a cyclically varying magnetic field, there are two ways to provide the periodic magnetic field change; using a pulsed magnet or moving of the magnetic material trough the fixed magnet. Either superconducting magnet or permanent magnet can be used.

In general, the Carnot cycle is hard to use above 20 K, because lattice entropy of magnetic material becomes considerably larger and this reduces the temperature change in adiabatic magnetization or demagnetization process. In that high temperature range, the Active Magnetic Regenerator (AMR) cycle has been developed. That method makes use of both the specific heat of the magnetic material and the magnetocaloric effect. In particular, it is essential for room-temperature magnetic refrigeration.

3. Environmental and energy applications

The magnetocaloric effect provides uniform heat change through the magnetic material with very short period within 1 millisecond order, so it is, in principle, possible to employ reversible refrigeration cycles such as the Carnot cycle. Also
using the solid material and simple electric control give advantages to realize a compact, light weight and high efficient cooling system. Furthermore, the magnetic refrigeration does not use global warming or ozone depleting refrigerant, so such environmentally friendly aspects have been attracted attention recently for their potential as room-temperature refrigerators.

Adiabatic demagnetization refrigerators have already been practically developed for space application to cool the sensors at ultra-low temperatures. A continuous ADR system consisting of four magnetic cooling units coupled in series gives very high performance of 20 $\mu$W (50mK) with the Carnot efficiency of 50%.

For the room-temperature range, magnetic refrigerators for air conditioner or refrigerator are being developed. AMR cycle refrigerators using permanent magnets and Gd spheres have been developed that yield refrigeration capacities of 200W or more. The coefficient of performance (COP) at that stage is around 3, which brings most practical use in air conditioning. Refrigerators for the production of liquid hydrogen are also under development, with the aim of improving the efficiency of hydrogen liquefaction. Fundamental experiment showed liquefaction efficiency more than 50%.

4. Challenges for materials science

In general, large magnetocaloric effect is provided by large magnetic moments, so early stage study is mostly focused on the materials including large magnetic moments such as rare earth magnetic elements. In the second half of the 1990s, research topics shifted to first-order phase transition materials, such as Gd-Si-Ge series and La-Fe-Si series. These magnets combine magnetic interaction and structural transition, so they can yield large magnetic entropy changes even in relatively weak magnetic fields. For example, La-Fe-Si-series materials are reported to produce three times as much magnetic entropy change as Gd, at the room-temperature in a 2T of magnetic field.

The conditions for selection of magnetic materials are as stated below. It is important to note that, by the great progress made recently in research into magnetic refrigeration, the material development is in the stage which requires not only verification of the magnetocaloric effects but also practical research phase including aspects such as fabrication quality control, mechanical strength and cost.

1) The magnetocaloric effect must be large. That means the magnetic entropy change due to external magnetic field must be large.
2) The material must have a suitable magnetic transition temperature. The magnetocaloric effect is generally greater near the magnetic transition temperature. As it is difficult to cover a wide refrigeration temperature range with a single magnetic material, it is necessary to combine several materials according to desired temperature range.

3) Hysteresis must be low. Soft magnetic materials are necessary for effective use of external magnetic fields.
4) High thermal conductivity. That is effective in faster the refrigeration cycle and larger the heat transfer efficiency.
5) Workability. The material must be formed into spheres or finned shapes to increase thermal efficiency. For example, spherical magnetic materials with diameters of 0.5~1.0mm are typically used in AMR systems. It is not uncommon for materials to have strong magnetocaloric effects but fail to reach the level of practical application due to poor workability.
6) Electrical resistance. As the magnetic material is placed in a variable magnetic field, it is necessary to suppress heating by eddy currents.
7) Chemical stability. For example, in magnetic refrigeration of hydrogen, the material could come into contact with hydrogen, so effects such as absorption and weathering must be avoided.

References

Magnetic refrigeration materials (high-temperature range) and systems:

Commentary:
6.4 Permanent Magnetic Materials

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1. Sintered magnets

The greatest application for permanent magnetic materials is in industrial motors. It has been estimated that 50% of all the electrical power consumed in Japan is used in motors, so if the development of high-performance magnets improves motor power consumption by just 1%, the saving in power consumption would be equivalent to the output of a small nuclear power plant. Modern cars use between 25 and 30 motors, so permanent magnets are an important industrial material for the auto industry. Use of hybrid electric vehicles (HEV) is becoming widespread as a means of reducing CO₂ emissions, and a further transition to electric vehicles (EV) is anticipated, but the magnets in vehicle drive motors get heated to around 200 °C when in use. Therefore, magnets, in particular Nd-Fe-B based magnets, are highly temperature-dependant, dropping sharply with rising temperature, so to use them at 200 °C requires magnets with coercivity of around 30 kOe at room temperature.

Figure 6.4.1 shows the energy product (BH)ₘₐₓ, coercivity Hₖ, and the basic magnet composition for Nd-Fe-B based sintered magnets in each application. The maximum standard for (BH)ₘₐₓ of commercial magnets shipped to the market today is around 50 MGOe, but the coercivity of magnets with high energy product is low, at around 10 kOe. In applications which require high coercivity, Nd is replaced with rare earth elements such as Dy, raising magnetic crystalline anisotropy as the (Ndₓ, Dyᵧ)₂Fe₁₄B phase. But Dy has the property of forming anti-ferromagnetic magnetic couplings with Fe and Nd, so adding Dy reduces the magnetization of the compound. Therefore, magnets for use in HEVs replace 40% of Nd with Dy to achieve high Hₖ, at the cost of reduced (BH)ₘₐₓ.

Recently, there has been a further problem, due to unstable supplies of rare earth elements such as Dy. The reserves of Dy are small, and if magnets containing Dy above the natural Dy/Nd ratio of ~0.1 are manufactured in large quantities for HEVs and EVs, it will become extremely difficult to obtain Dy. Furthermore, rare earth elements such as Dy are concentrated in China, so prices are already rising due to the Chinese government’s policy on the export of rare earth elements. The natural occurring ratio of Dy to Nd is around 10%. Nd-Fe-B based sintered magnets must be developed which achieve coercivity of 30kOe with Dy usage at half or less of the current level. The high-performance magnets used in vehicle motors are Nd-Fe-B based sintered magnets. The actual magnetic compound is slightly richer in the proportions of Nd and B than the stoichiometric combination of Nd₂Fe₁₄B. Therefore, as Figure 6.4.2 shows, the surplus Nd forms thin, Nd-rich phases on the boundaries of crystalline grains, completely covering Nd₂Fe₁₄B crystalline grains of around 5 μm, leaving them magnetically isolated, to develop coercivity. In commercial magnets, the basic mix is Nd-Fe-B, with trace quantities of added Cu and Al, but the coercivity that can be achieved by this kind of three-element compound is no more than 12kOe. The theoretical limit of magnet coercivity is the anisotropic magnetic field Hₐ=2K₁/Mₘ, which is equivalent to the field at which a single-crystal magnet with crystalline magnetic anisotropy K₁ becomes saturated in rotational magnetization, so the 12kOe coercivity of an Nd-Fe-B sintered magnet reaches only 16% of the 73kOe anisotropic magnetic field of Nd₂Fe₁₄B. If coercivity equal to at least 50% of Hₐ could be achieved, it would be possible to make magnets with coercivity of 35kOe at room temperature without a major sacrifice of energy product (BH) (blue arrow in fig. 6.4.3). That is the reason for the rush of research work into ways of raising the coercivity of current sintered magnets without using Dy or other rare earths.

The reason why the coercivity of sintered magnets reaches no more than 16% of Hₐ is, as Figure 6.4.1 illustrates, when a field is applied in the reverse direction after magnetization reaches saturation, reversed magnetic domains appear from the boundary in a field far weaker than Hₐ. Even in materials with high crystalline magnetic anisotropy, there is almost no coercivity where there are no domain pinning sites, such as in single phase single crystals or fully epitaxial coatings, so once reverse magnetic domains appear on grain boundaries, reversal of magnetization advances rapidly. Where there are protrusions on grain boundaries, it becomes easier for the crystal nucleation of reversed magnetic domains to occur in low external fields, due to localized demagnetization. Also, if crystalline magnetic anisotropy becomes locally low in some parts of the boundaries between Nd₂Fe₁₄B crystalline grains and the surface of the Nd-rich phase covering the grains, crystal...
nucleation begins in those parts, and reversal of magnetization occurs in low magnetic fields. On the other hand, if the Nd$_2$Fe$_{14}$B grains are entirely magnetically isolated by the Nd-rich phase, the probability of cores forming declines as the crystalline grains get smaller, while the coercivity increases. Coercivity is expected to reach its maximum at the single magnetic domain grain size. However, it is known that actual Nd-Fe-B sintered magnets achieve their maximum coercivity at crystalline grain sizes ten times larger than the single magnetic domain grain size, with coercivity declining rapidly at smaller sizes. Therefore, there appears to be scope for improving the coercivity of sintered magnets by further reducing the peak grain size which generates maximum coercivity, which can be achieved by controlling the structure of the boundary between the Nd-rich phase and the Nd$_2$Fe$_{14}$B grains, and by making the crystalline grain finer. On the other hand, if elements that enhance crystalline magnetic anisotropy by replacing Nd, such as Dy and Tb, could be restricted to only the boundary between the Nd$_2$Fe$_{14}$B and the Nd-rich phase, it would be possible to substantially raise the coercivity of sintered magnets with amounts of Dy usage below the naturally occurring Dy/Nd ratio. In fact, such attempts have succeeded by dispersing Dy and Tb from the lamina surfaces of Nd-Fe-B sintered magnets to the grain boundaries, but there are limitations on the magnetic lamina thickness to which this method is applicable, making it difficult to apply to bulk magnets. When an effective method is found for segregating Dy and Tb to the grain boundaries, it will be extremely effective in reducing Dy usage.

The magnet manufacturers are busily working on this kind of research to reduce the amount of Dy used in the high coercivity magnets for HEV and EV drive motors. In Nd-Fe-B sintered magnets, however, even if the usage of Dy can be reduced, large amounts of Nd would still be required, and the theoretical limit of 60 MGOe for energy product remains, so a long-term research effort will be required to overcome these limitations. Anisotropic nanocomposite magnets have the potential to greatly exceed the limitations of sintered magnets.

2. Nanocomposite magnets

Nanocomposite magnets are magnets in which nanostructures are developed as far as making exchange couplings between grains in soft phases with high magnetic flux density and in hard phases with high crystalline magnetic anisotropy. Such nanocomposite magnets use far lower concentrations of rare earths than the MQ grains of the Nd-rich mix used in conventional magnetic materials, so they are cheaper and have better corrosion resistance. Therefore, they are being developed commercially as raw material powders for bond magnets of medium characteristics. While the ability to gain medium magnetic characteristics even with reduced usage of the rare earths themselves is a characteristic of nanocomposite magnets, they will not surpass the characteristics of sintered magnets as long as they are isotropic.

If nanocomposite magnets could be made as anisotropic magnets with the axis of easy crystalline magnetization controlled into one direction, the angularity of the deGauss curve would be improved, achieving characteristics superior to current sintered magnets. That is the approach behind many experimental research projects aiming to achieve high $(BH)_{\text{max}}$ in soft/hard multilayer coatings, but when a soft-phase coating is formed on a continuous hard-phase layer without pinning sites, coercivity declines dramatically, so some method is needed for introducing pinning sites.

In the multilayer coating of Cr/[Sm(Co,Cu)/FeCo]$_5$ shown in Figure 6.4.3, the FeCo of the soft phase and the Sm(Co,Cu) of the hard phase form strong exchange couplings, creating anisotropic nanocomposite magnets with $(BH)_{\text{max}}$, having strong in-plane anisotropy. It is known that when the Co in SmCo$_5$ is replaced with Cu, coercivity increases, even in a uniform structure, so it appears that pinning sites are introduced by the change, for some reason. This multilayer coating exhibits strong in-plane anisotropy, with in-plane $H_c$=7.24kOe and $(BH)_{\text{max}}$ = 32 MGOe, comfortably surpassing the theoretical limit of $(BH)_{\text{max}}$ in SmCo$_5$ single-phase magnets, which is 28.8 MGOe. Furthermore, $(BH)_{\text{max}}$ for SmCo$_5$ and Sm(Co,Fe,Cu)$_5$ sintered magnets is 20–28 MGOe, so even the $(BH)_{\text{max}}$ of sintered magnets with high characteristics is surpassed. That result is the first to demonstrate a nanocomposite magnet that surpasses the theoretical limit for single-phase magnets. From this result, we can conclude that if Nd$_2$Fe$_{14}$B, which has saturated magnetization higher than SmCo$_5$, could be used to create an anisotropic nanocomposite magnet with Fe, it would be possible to develop a high-performance magnet that would surpass the theoretical limit of 64 MGOe for Nd$_2$Fe$_{14}$B. Of course, many technical difficulties must be overcome before anisotropic nanocomposite magnets of ideal bulk could be produced on industrial scale, but if the nano-scale structure of Nd$_2$Fe$_{14}$B, currently the magnetic compound with the highest degree of magnetization, could be controlled, it would potentially create a magnetic of even higher characteristics.

It is difficult to introduce pinning sites in Nd$_2$Fe$_{14}$B phases, so a method must be found for nanostructure control to improve saturated magnetization in the soft phase without reducing coercivity.

3. Summary

Despite the importance of permanent magnetic materials as environmental and energy-related materials, technical innovation was receding as enthusiasm for research cooled off. In recent years, production of Nd-Fe-B-based magnets has shifted to China, due to problems of resources and manufacturing costs. Considering the importance for industry, and particularly for the manufacture of environment-friendly vehicles, we cannot afford to abandon magnet research, once the preserve of Japanese technology, so easily. If the technical innovations summarized in this paper could be achieved, there is the possibility of developing permanent magnetic materials able to solve resource problems.

References
1. Basics of the material

Shape-memory alloys are materials which convert heat into mechanical energy and output it. The characteristics that are practically important are shape memory effect and superelasticity. The principles behind their action are similar as shown in Figure 6.5.1. When the alloy is cooled to below the transformation temperature, the crystal structure changes. At that time, variants with the same lattice but different orientations (in the relationship of A and B in the diagram) are formed in the same proportions, so the deformations of the lattices cannot be discerned on the macro scale. But when a force is applied, lattice B is converted into lattice A. In that case, the deformed shape does not return even when the load is removed. However, when the material is heated, the lattice regains its square shape (high-temperature phase), so the material also returns to its original shape. That is the shape-memory effect, and the force of the material’s reversion can be used to do work. On the other hand, if the high temperature phase is deformed at a stable, high temperature, the material reverts to the original shape as soon as the load is removed (superelasticity). If repeated deformations are required, the material is used under a suitable load (called the bias force), so that it deforms at a low temperature and reverts at a high temperature.

2. Research trends

TiNi alloy, which has already been practically developed and is known as a functional material, is widely used, and research is under way into new manufacturing methods and processing techniques, to suit applications. Promising applications for the future include thin film actuators for medical treatment equipment and MEMS, and smart materials in combination with plastics and other materials.

The operating temperature of TiNi alloy is up to 100 °C, but once it is made usable in the 100–200 °C range, its usefulness would extend beyond civil applications to vehicle engines and the generation field, including nuclear power. It is expected to save energy, among other uses. Therefore, research is under way into alloys with a third element added, and also into materials based on platinoid elements that could be used in gas turbine environments at 1,200 °C.

While the medical applications of TiNi alloy expand, many of those involved in medical care are concerned over the allergenicity of Ni. Another area of research which has been vigorously pursued in recent years, for the substitutes of TiNi alloys, is Ti-based alloys in which additives such as Nb or Mo are added to the Ti, to stabilize the β phase, followed by Zr, Ta, Sn, Sc, to strengthen the alloy and adjust the transformation temperature. These alloys are easily workable, and expectations are high for their future applications.

The characteristics of Fe-based shape-memory alloys, which are regarded as difficult to use in practice, are improving. If they could be manufactured cheaply, they would be used in great quantities, as a construction material, among other applications.

The response speed has been regarded as a shortcoming of shape-memory alloys, but extensive research is now under way into magnetic field actuated shape-memory alloys, which have far better response speeds.

3. Applications to the environment and energy

3.1 Energy-saving actuators for a comfortable living environment

Shape-memory alloys are intelligent materials, which combine sensor functions with actuator functions. If both functions can be used at the same time, they could use heat energy present in the environment, rather than requiring external electrical energy, to perform work without other input. They also serve as clean actuators, with no operation noise, so they can be used with peace of mind in locations closely linked to the living environment. One example is underfloor ventilators using shape-memory alloy. Shape-memory alloy is used to open and close ventilation holes so that the holes are opened as the temperature rises, taking air into the underfloor space, but they are closed automatically as the temperature drops, shutting out cold air. Absolutely no electricity is used, so it is an energy-saving technology, friendly to people.
and the environment.

3.2 Low-temperature thermoelectric generation

Power generation technologies are being researched which will make more active use of the energy conversion functions of shape-memory alloys. Low-temperature heat sources, such as factory waste heat, geothermal heat, seawater temperature gradients and solar heat, which have been discarded or left unused in the past, can be used to make clean engines that emit no CO₂. Figure 6.5.2 shows an example of an offset crank engine, in which a coil formed of shape-memory alloy extends and contracts repeatedly in air and in warm water, running continuously for as long as there is a heat source.

3.3 Recycling technology

Resource saving and recycling technologies, focused on the intelligent properties of shape-memory alloy, are also under development. Figure 6.5.3 shows a washer which uses the shape recovery function to facilitate disassembly work. The structure of the washer is such that when the equipment comes to the end of its service life, hot water is applied to each case, causing the washers to open and the screws to drop out of the covers. That has succeeded in facilitating disassembly and making recycling operations more efficient.

4. Challenges in materials science

80% of the shape-memory alloys currently used are TiNi alloys. For responding to the environmental and energy problems in a wide field, it is necessary to develop novel alloys and extend their applications based on the foundation of materials science.

1) Development of high-temperature shape-memory alloys: A number of alloys have been proposed, but they have problems of price, characteristics and other attributes, and none of the materials is practically usable at 100 °C or more. It is necessary to search for new alloy systems, and to improve mechanical characteristics at high temperatures.

2) Development of cheap shape-memory alloys: Fe-based alloys are cheap materials, but their characteristics are inferior to TiNi alloy. Therefore, research is necessary to improve the shape recovery rate, using precipitation hardening etc. A material usable cheaply and in large volumes would be applicable as a damping material.

3) Development of shape-memory alloys which do not contain Ni: Ni-free, Ti-based shape-memory alloys would require increased deformation strain and improved reliability. Heat treatment and control of texture would be effective for strengthening the material. The material would be easily workable and have many solid solutes, so it would also be possible to search for new alloy compositions.

4) Broader application: Thin films and wires would enable the high response speed of actuators. It has also become clear that the use of fabrication methods other than casting would yield finer structures with superior shape-memory characteristics. It is necessary to clarify the effects that nano-order structures have on characteristics, and use them in alloy development.

5) Clarify the mechanism of martensitic transformation: Progress in experimental techniques is revealing the details of martensitic transformation, which is the origin of the shape-memory effect. It would be effective, for the development of new materials, to take research back to the basis of the transformation.

Reference

1) http://www.nedo3r.com/TechSheet/JP-0522.htm

Those who want to learn more about shape-memory alloys should refer to:

1. Introduction

Friction is an important phenomenon, closely involved in everyday life, and technologies to use strong friction, or conversely, to reduce friction as far as possible, have been researched since ancient times. When the flat upper surface of body A and the flat lower surface of body B are in contact, and A is anchored and B is made to slide, a force acts to resist the movement. That is the force of friction. At that stage, the ratio between frictional force $F$ generated on the contact surface and the force $N$ pressing body B onto body A is the coefficient of friction $\mu$, which completes the formula below.

$$F = \mu N$$  \hspace{1cm} (1)

If $\mu$ can be made smaller, the energy lost to friction is reduced, so the development of materials which achieve low friction, which are highly lubricant materials, is essential for energy saving. But is there such a thing as low-friction materials with such extremely small $\mu$ values that the energy lost to friction drops to almost zero?

C$_{60}$, which is a molecule consisting only of carbon atoms, and a type of Fullerene, has a spherically symmetrical form with a diameter of 0.72nm. C$_{60}$ forms molecular crystals coupled by weak van der Waals forces, but the C$_{60}$ molecule itself is very hard and has an extremely high bulk modulus of 717GPa, far surpassing that of diamond $^1$. The density of C$_{60}$ crystals is approximately 1.7g/cm$^3$, which is very light, being 1/4 that of iron, 7.9g/cm$^3$. The coefficient of friction of thin coatings of C$_{60}$ formed by the sublimation method is in the range 0.08~0.18, which is as low as molybdenum disulfide or graphite coatings $^2$. For that reason, C$_{60}$ is expected to serve as the ultimate ball bearing. This paper describes how C$_{60}$ could be used in the field of friction and abrasion.

2. Research trend

2.1 C$_{60}$ intercalated graphite

Miura et al. have reported, as described below, that C$_{60}$ intercalate graphite has a coefficient of friction close to zero $^3$. When a block of graphite is agitated in a mixture of nitric and sulfuric acids, then washed with pure water, and then heated in a kiln at 1050 °C for a short period, the distance between graphite layers can be increased by a factor of tens. This expanded graphite and C$_{60}$ powder are vacuum sealed into a silica tube and heated in a kiln at 600 °C for 15 days. The result is graphite with C$_{60}$ between the layers, which is C$_{60}$ intercalated graphite. In this compound, layers of single C$_{60}$ atoms alternate with graphite layers, stacked with a pitch of 1.3nm between layers.

When C$_{60}$ intercalated graphite film produced by that process was analyzed using a friction microscope, the frictional force, which is the horizontal force, was observed to be almost zero under an applied load of up to 100nN. Figure 6.6.1 illustrates a friction measurement test on C$_{60}$ intercalated graphite film using a friction microscope probe.

C$_{60}$ intercalated graphite has the potential to greatly reduce frictional energy losses from previous levels, so it can be expected to make a great contribution to solving energy problems as applications are developed.

2.2 Micro-rails of fullerenes

One of the key points of the C$_{60}$ intercalate graphite described above is that it is highly fluid, due to the rolling and shaking of the spherical C$_{60}$ molecules. The C$_{60}$ inside C$_{60}$ nanowhiskers (C$_{60}$NW), which are one kind of fullerene nanowhisker (FNW), is normally loosely coupled by van der Waals forces, provided it is not treated with UV light or electron beam $^4, 5$. C$_{60}$NW has a lattice constant of the same size as face-centered cubic crystals of C$_{60}$ at normal temperature and pressure, so individual C$_{60}$ molecules are able to roll freely. C$_{60}$NWs are single crystalline semiconductor nanofibers and between the orders of micrometers and millimeters in length. Their diameter is a constant (approximately 100~1,000nm) along the axis of growth.

Figure 6.6.2 shows a C$_{60}$NW (diameter 526nm) that would normally be straight, bent with a radius of curvature of 29µm. The surface of C$_{60}$NW is flat, on a molecular scale, and the superior lubricant properties of C$_{60}$ suggests that C$_{60}$NW could be used as...
a sliding material with low coefficient of friction.

C₆₀NW can be bent with a small radius of curvature and has a uniform diameter, so it could be used to form low-friction micro-rails in MEMS (micro electro-mechanical systems) devices.

### 2.3 Lubricant functions of C₆₀

In early research, Hisakado et al. have reported that alcohol with a 1% addition of C₆₀ powder provides superior effects against friction and abrasion of ceramics such as Al₂O₃, SiC and TiC\(^{6}\).

The surfaces of gears, ball bearings, other bearings and similar components are coated with mineral oil for lubrication. Attempts are under way to improve the performance of mineral oil by adding fine powder of C₆₀, with 10nm average diameter\(^{7}\). Lee et al. have performed friction experiments with an addition of 0.01~0.5vol% of C₆₀ to mineral oil. Results indicate that the coefficient of friction of oil with C₆₀ added is smaller than that of oil without C₆₀. Experiments using disk-on-disk frictional wear testing equipment indicated that increasing the amount of added C₆₀ progressively reduced the amount of friction.

### 3. Summary

The above demonstrates that fullerenes are a superior lubricant. As fullerenes are expensive, development of applications is expected to proceed in fields such as machine oil additives, in which the addition of a small amount can yield major improvements in lubricant properties, and solid lubricants for micro-devices.

### References

6.7 Light structural materials

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1. Basics of the materials

The basic characteristic of structural materials is to have the ability to support a large load safely. The resistance against plastic deformation is the yield stress, and that towards fracture is the tensile strength. As the yield stress and the tensile strength increase, a load that a material can support increases. The unit for yield stress and tensile strength is Pa=N/m^2, force per unit area. Therefore, if materials show a constant yield stress, the weight of the material parts that support a given load can be decreased when the density of a material is small. This index is referred as specific strength = yield stress/density.

Steel is the most highly used material among structural metallic materials. Metallic materials that have a lower density than this steel are generally called light metals or light structural materials. Table 6.7.1 shows that magnesium has the lowest density among the structural metallic materials and is one fourth that of steel. The density and the elastic modulus are properties that only depend on the chemical composition; however, the yield stress and the tensile strength are a structural sensitive property, they depend on the metallic crystal structure and the microstructure in addition to the chemical composition. Microstructure control can increase the yield stress of steel to exceed 800 MPa and has led to the development of high tensile steels with a specific strength of over 100MNm/kg. Table 6.7.1 shows the relationship between the yield stress and the specific strength of metallic materials. In this paper, we describe the trend of light structural materials including steels with a specific strength of over 100MNm/kg.

2. Environmental issue and light structural materials

The dominant contribution of light structural materials towards environmental issue in Japan is the reduction of carbon dioxide by the improvement of fuel consumption of vehicles. For example, a 10% reduction in the weight of an automobile improves the fuel consumption by 5%. The weight of the new model automobiles that are successively being put on the market, however, will gradually increase unless efforts are taken to decrease their weights. The reason is that improvements in collision safety and the rigidity of the vehicle are made along with the development of each new automobile model, and reinforcements are added to strengthen the vehicle and to improve the function of absorption and the dispersion of the impact energy on collision.

When Kyoto protocol was issued in 1997, the Japan Automobile Manufacturers Association, Inc. (JAMA) made a commitment to a carbon dioxide emission of 120g/km for a 1 km mileage in 2012. Therefore, in addition to an improvement in engine efficiency, a reduction in the weight of the vehicle becomes an essential problem for reducing the amount of carbon dioxide emission.

The April 4, 2008 edition of various newspapers reported the domestic new automobile model sales ranking. Honda “Fit” regained its top position in all the categories with the exception of light weight vehicles by a margin of 879 cars over Toyota “Corolla”. Excluding light weight vehicles and hybrid cars, the New Fit was reported to have the lowest fuel consumption (24km/L). Since the carbon dioxide emission per 1L of gasoline is 2.31kg, with this fuel consumption, the carbon dioxide emission per 1 km mileage is 96g/km and achieves the JAMA’s target for 2012 (120g/km for a 1 km mileage). The expanding application of light structural materials markedly contributed to the fuel consumption improvement of this automobile.

3. Research trends for materials development

Specific strength must be increased to decrease the total weight of the materials used. The mechanical characteristics of various metallic materials appear on page 382 of the 2008 edition of the Chronological Scientific Tables (Maruzen), a literature that can
be cited easily in Japan. Table 6.7.2 shows an excerpt. The materials on this list include steels with a yield stress of over 1400 MPa and aluminum (A7075) of over 500 MPa. In terms of specific strength, they exceed 150 MNm/kg and can be classified as a light material that is 10 times lighter than industrial pure iron of a specific strength of 12 MNm/kg.

### 3.1 Improvements of formability

Numerous material related problems arise when we intend to reduce the weight of the vehicle by employing the high specific strength materials, light materials. The first problem is of course the cost. Titanium alloys are typical light materials with superior characteristics, but seldom to be applied in vehicles because of its high cost. Even in the aircraft field, expensive titanium alloys are employed mainly to military planes. The second problem is deterioration of formability. As shown in table 6.7.2, the elongation decreases as the yield stress increases. Elongation is measured by dividing the increase in the sample length till a material fractures using the tensile test by its initial length. With larger elongation, a material can take on various additional forms by plastic deformation. In general there is a trade-off relationship that as the specific strength or yield stress increases, the elongation decreases. Many automobile parts are produced by employing a plastic deformation called press forming; therefore, increasing the elongation is being demanded despite its high strength. This is a challenging issue to be overcome. Microstructure control using nanotechnology is being carried out for this type of scientific encounter. For the processing of high strength materials, many other problems remain in such areas as machinability and weldability.

### 3.2 Reduction of rare metals

Microstructure control through phase transformations is one of promising ways to improve mechanical properties of metallic materials. The phenomena of phase transformations are largely influenced by alloy elements; therefore, alloying has been a major pillar in the development of metallic materials. Small amounts of rare metals such as niobium (Nb) and molybdenum (Mo) have been commonly added to steels to obtain the microstructures that increase the strength with a sufficient elongation. Now, a more sophisticated microstructure control without using these rare metals is being demanded because of resource rack of these metals.

In addition to the improvement in fuel consumption in automobiles, light metallic materials with high strength and elongation are always needed to improve safety in transportation, enhance architectural flexibility in construction, and improve performance in heavy machinery.

### References


For further reading
Due to the ever increasing demands on oil and the resulting increase in the price, the improvement of specific fuel consumption (SFC) has become the hottest issue in aeroengine industries and airline companies. The improvement in SFC is required also for the CO₂ reduction to mitigate global warming. Fig. 6.8.1 shows an improvement in SFC in the last 40 years. Further improvement is still needed for the next generation airliners and, to realise this, new materials especially materials with high temperature capabilities are desired for increasing peak temperature of Carnot cycle of the engine.

Ni-base superalloys have been used as most of the turbine components. Among them, Ni-base single crystal (SC) superalloys are the materials being used as the first stage blades in high-temperature turbines where the operating temperature and the stress are the highest. Fig. 6.8.2 shows the history of improvement in temperature capability of Ni-base superalloys. The “Target” shown in this figure is that of the “High Temperature Materials 21 Project ” being conducted in NIMS (Phase 2: 2006-2010). Typical chemical compositions of Ni-base superalloys for turbine blades are also presented in Table 6.8.1.

![Fig. 6.8.1 A History of Improvement in Specific Fuel Consumption of Aeroengins.](image)

![Fig. 6.8.2 History of improvement in temperature capability of Ni-base superalloys.](image)

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Table 6.8.1 Chemical Composition of Ni-base Superalloys for Aeroengine Turbine Blades (wt%, bal. Ni).
Ni-base superalloys evolved from forged/wrought alloys to conventionally cast (CC) alloys, directionally solidified (DS) alloys, and then single-crystal (SC) alloys. Single crystal superalloys have also evolved from 1st generation (0Re) to 2nd generation (2-3Re), 3rd generation (5-6Re), 4th generation (5-6Re and 2-3Ru), and then 5th generation (5-6Re and 5-6Ru) alloys. So far 1st to 3rd generation SC superalloys are used practically, typically CMSX-10\(^2\), a 3rd generation alloy, in the latest fan jet engine Trent 900 used for Airbus 380. The 4th generation alloys have been developed in the US, France and Japan. The highest temperature capability, 1100 °C, has been reached by NIMS with 5th generation alloys TMS-162 and TMS-196\(^3,4\), which are the only 5th generation alloys available at present in the world. In NIMS superalloys, especially 4th and 5th generation alloys, an interfacial dislocation network on \(\gamma\) and \(\gamma'\) phases are designed to be finer (20 nm) to prevent dislocation cutting through the interface to suppress creep deformation.

When Ni-base superalloys are used as turbine blades in the high-temperature turbines, thermal barrier coatings (TBC) and air cooling systems inside the blades are essential, as shown in Fig.6.8.3. As a new development in this field, in 2006, “EQ coating” was invented as a bond coat material at NIMS\(^5\). Because of the composition carefully designed to be in an equilibrium state with the substrate superalloy, the interface can maintain the phase stability for the entire life of the blade, eliminating the usual problem so-called secondary reaction zone (SRZ) causing shorter life of the blade.

As the turbine temperature increases, the temperature capabilities of turbine discs, which are produced through cast and wrought (C&W) or powder metallurgy (P/M) processes, are also required to be improved. Fig.6.8.4 shows the improvement of turbine disc superalloys in terms of tensile strength at 650 °C\(^6\). Here, TMW-4 is a C&W Ni-Co-base alloy developed in NIMS\(^7\), exhibiting same property as P/M processed alloys. Because of the lower process cost with C&W, TMW-4 alloy has a highest cost-performance compared with other disc superalloys.

So-called alternative materials to Ni-base superalloys are also being investigated. Ir or Pt group metals base “refractory superalloys”, composed of \(\gamma\) and \(\gamma'\) phases as Ni-base superalloys have been proposed by NIMS\(^8\). They have potentials for ultra-high temperature use, because of the high melting points and useful creep strength even at 1750 °C, as well as the better oxidation property than conventional refractory metals and alloys based on W, Mo, Ta, and Nb. The cost and density are the factors to limit the range of applications. Nb/Nb-silicide and Mo/Mo-silicide base alloys are also widely investigated. Cr-base alloys also have an attention. Cr-Re and Cr-Ag alloys with good ductilities for structural materials have been reported\(^9\). In spite of these activities, it is fair to say that it will take a long time for these alternative materials to possibly substitute the Ni-base superalloys, except that TiAl base alloys are planned to be used as low-pressure turbine blade materials for weight reduction.

References
Chapter 7. Nano-driven Energy/Environmental Materials

7.1 Overview

In current nanotechnology research, the search for and research into the creation of new materials and substances with a strong sense of scale, from the molecular and atomic level to sizes on the nanometer order, is being conducted and various developments are being made. Various studies are being performed with the purpose of having these new developments in materials science made through this nanotechnology serve useful roles in solving various problems in the fields of the environment and energy such as saving energy, reducing impacts on the environment and finding alternatives for scarce natural resources. In this chapter, we have organized these into four approaches (see Fig. 7.1.1).

(1) New phenomena and functions on the atomic and molecular level
(2) Development of new functions for nanoscale substances
(3) Fabrication of new materials by nanoassembly technologies
(4) Fine control of nanostructures

Regarding (1), with rapid progress in technologies that permit single electrons or molecules to be individual manipulated typified by the scanning probe microscope, it is now possible to approach phenomena and properties of materials that had been impossible up until now, and as a result, atomic switches and molecular electronics have been proposed. These proposals have the promise of permitting extremely fast operation with extremely low power consumption, among other advantages.

Regarding (2), with the discovery and synthesis of nanotubes, nanorods, nanosheets, nanoparticles and many other new substances that have various sizes and dimensionalities, new functions deriving from the size effects and unique shapes have now been expressed. For example, high-efficiency electron emission and hydrogen storage are possible with nanotubes, while superior electronic and magnetic functions are achieved with nanosheets, so the exploration of a wide range of application is proceeding.

Regarding (3), through the development of techniques for the integration and creation of arrays of organic-inorganic nanomodules, a wide variety of materials can now be designed in the sense of “assembling them from parts” and as a result, it is now possible to develop advanced functions that would be difficult to achieve with a single substance, and the realization of high efficiency in energy conversion elements is expected.

Regarding (4), by achieving fine control of the types of atoms and their arrangement within an inorganic crystal lattice, the control of materials and substances that take advantage of nano/meso scale porous structures, and the control of the degree of dispersion of nanoparticles, clusters or the like within a medium become possible along with an extremely wide range of other technologies.

This chapter presents novel functions that have been achieved by means of the four approaches described above, along with the trends in work in recent technologies that aims to make contributions to the environment and energy sectors.
7.2 Atomic Switch Materials

1. Basics of materials

An atomic switch refers to a switch element that operates by utilizing an oxidation-reduction reaction to control the formation or dissipation on the atomic scale of a metallic filament formed between electrodes. In atomic switches, ion conductors are used as the main materials. Ion conductors can be divided into solid electrolytes wherein ions alone contribute to conducting electricity and electron/ion mixed conductors where electrons also contribute to conducting electricity.

Fig. 7.2.1 presents a schematic diagram of the basic structure of an atomic switch. The switch has a M₁/M₂ structure comprising a metal (M₁)/ion conductor (I)/metal (M₂), where a metal that is soluble as ions within the ion conductor (M₁) is used as one of the electrode materials. When a positive voltage is applied to this electrode, a metal oxidation (ionization) reaction occurs at the interface between this electrode and the ion conductor, so metal atoms (M₁) become metal ions (M₁⁺) and dissolve into the ion conductor. The metal ions (M₁⁺) diffuse within the ion conductor toward the side of the opposite-electrode metal (M₂). As a result, the metal ion concentration in the vicinity of the opposite electrode increases until it becomes supersaturated, and the metal ions that can no longer remain dissolved within the ion conductor are reduced and precipitate out as metal atoms. These precipitated metal atoms form a filament between the electrodes and the switch turns on. On the other hand, when a voltage of the opposite polarity is applied, an oxidation (ionization) reaction occurs within the precipitated metal atoms, and thus the filament is dissolved and the switch turns off.

The operating properties (operating voltage, operating speed, etc.) of the atomic switch are determined by the threshold voltages for the oxidation/reduction process, the rate of these reactions as well as the rate of diffusion of metal ions through the ion conductor and other factors. The values of these properties depend greatly on the ion conductor materials and metal electrode materials used, as well as the combinations thereof.

2. Research trends

Development is proceeding on phase change memory, magnetoresistance memory, resistive random access memory, atomic switches and other new devices that may serve as substitutes for semiconductor devices that have reached the extremes of miniaturization. Each of these devices is characterized by having a simple device structure and being a nonvolatile state device, so they have properties not seen in ordinary semiconductor devices.

Among these, the atomic switch achieves the switched-on state by means of a metal filament, so it is characterized in having a smaller resistance in the switched-on state than the other devices. It is suitable for the application to low power consumption and high-speed signal transmission circuits. As one example of device development taking advantage of these characteristics, let us present its application to the switching circuit of a programmable logic device.

When an atomic switch is used, it is possible to shrink the surface area of a switching circuit to 1/30 of that of a conventional circuit, so it is possible to incorporate many switches into a single chip (Fig. 7.2.2). As a result, it is becoming possible to develop devices that can achieve many types of functions on a single chip.

The operation of the atomic switch was initially confirmed using a sulfide system as the ion conductor, but recently its opera-
tion has also been confirmed in a metal oxide system that can be more easily embedded into semiconductor devices.\textsuperscript{5)}

### 3. Applications to energy and the environment

While electronic devices serve an important role in supporting today’s information-intensive society, the power consumed when they operate and the energy required to manufacture them are large, so the fact is that they place a large burden upon the environment. For this reason, the development of devices that can be manufactured at low energy costs and that can operate with low power consumption is a major problem in achieving both the sustainable expansion of the information-intensive society and an energy-saving society.

The atomic switch has a simple structure, so it can be fabricated by a manufacturing process that is roughly one-fourth as complex as that for a semiconductor device. In addition, its operating power can also be reduced to roughly a nanowatt, and thus it has a good prospect for being able to solve this problem.

### 4. Challenges in material science

The basic mechanism of operation of the atomic switch is the formation or dissipation of a metallic filament by means of a solid-state electrochemical reaction. However, the reaction process on the atomic level has not been fully elucidated. In order for it to be used widely as a device in the future, it is necessary to be able to design and control freely its operating voltage and other device characteristics. In addition, evaluation of its durability and reliability are also essential in the course of commercialization. With atomic switches having a principle of operation that differs from that of semiconductor devices, it is not even known as to whether or not the same evaluation techniques can be used as with semiconductor devices.

Among resistive random access memory devices that have the same device structure as atomic switches, there are some wherein the transmission path (filament) is thought to be formed by oxygen loss. Elucidating a unified mechanism that includes these devices will be necessary in order to proceed with the commercialization of new devices to replace semiconductor devices. The challenges in materials science may be summarized as follows.

1) It is necessary to fully elucidate the mechanism of operation based on an elucidation of the solid-state electrochemical reactions and metal ion diffusion process on the atomic level, and also establish device design/control techniques based thereupon.
2) Accelerated lifetime test methods and other evaluation techniques must be developed with a view toward commercialization.
3) Material-dependent mappings of device characteristics must be prepared in order to handle diverse applications.
4) Research into integration processes and materials must be conducted with the objective of early commercialization based on embedding with semiconductor devices.

### References

1. Introduction

Nanosized and low-dimensional (low-D) materials, in which structure, composition and morphology are controlled on the nanoscale, exhibit unique physical and chemical properties different from those of conventional bulk materials. For this reason, the creation of novel nanomaterials are attracting substantial interest as fundamental technologies that will produce breakthroughs in various fields such as electronics, energy and environment.\(^\text{(1,2)}\)

A major impetus of such nanomaterials research was the discovery of fullerenes (C\(_{60}\)), carbon nanotubes (CNT) and other carbon nanomaterials. In inorganic cases, recent progress in synthesis techniques has lead to the successful fabrications of various nanomaterials and nanostructures such as nanoparticle, nanoclusters, nanorods, nanotubes, nanosheets (Table 7.3.1), opening up a new emerging filed for the nanotechnology in metal, semiconductor and oxide systems. Such nanomaterials are not only interesting as new functional materials, but also attracting considerable attention as key materials for creating more complex nanoarchitectures using them as fundamental building blocks.

Table 7.3.1 Structures and morphology of nanoscale materials

<table>
<thead>
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<th>0D structure (Sphere)</th>
<th>1D structure (Wire)</th>
<th>2D structure (Sheet)</th>
<th>3D structure (Bulk)</th>
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<td>Nanosheets</td>
<td>Nano ceramics</td>
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<td>Nanowires</td>
<td>Nanobelts</td>
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<td>dots</td>
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<td>Quantum wells</td>
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</tbody>
</table>

C\(_{60}\) diameter: 0.7 nm  
Diameter: 1 nm to dozens of nm  
Thickness: several nm  
3D structure, bulk structure

2. Recent research trends

In carbon nanomaterials, recent progress in mass-production techniques has lead to their practical applications. For example, CNTs have been applied to a broad range of practical devices such as transistors, capacitors and fuel cells for mobile equipments. In inorganic nanomaterials such as metals, semiconductors and oxides, current interest concerns about the creation of functional nanostructured materials by controlling material composition, organization, structure and surface boundary on nanometer order. Particularly, research of transition metal oxide nanomaterials has achieved a marked progress in recent years, and various functional nanomaterials of new forms have been reported. Those include 0D (nanoparticle, nanocluster), 1D (nanorod, nanowire) and 2D (nanosheet, nanobelt) systems in wide-gap semiconductors, ferroelectric materials, ferromagnetic materials. These oxide nanomaterials are exceptionally rich in both structural diversity and electronic properties, with potential assembly into various functional nano-devices.

Moreover, one of hot topic in nanomaterials is the successful fabrication of graphene which is an atomically thin carbon nanosheet.\(^\text{4)}\) Theoretical works on the graphene has a long history, and the graphene sheet had been predicted to exhibit superior electrical, mechanical and thermal characteristics arising from its unique two-dimensional structure. However, due to the difficulty of its synthesis, the graphene had remained an unexplored frontier in carbon materials. After the successful exfoliation of the graphene sheets, research in such 2D systems has recently intensified, and there are tremendous reports on exotic properties such as 2D electron gas, high electron mobility, quantum hole effects and half metal.

3. Applications in the fields of energy and environment

In recent years, research on nanomaterials has been proceeding toward application phases in various fields such as electronics, energy and environment. In these applications, a common advantage of the use of nanomaterials is the environmentally-benign aspect with low consumptions in energy and resources. These features are thought to be extremely important for a future sustainable society.

In the researches of energy and environment applications, current focus is placed on the creation of nano-ordered functional or structural materials with advanced physical properties for energy savings, which contribute to environmental improvement and conservation. In this context, there have been many reports on the creation of functional nanomaterials/nanosystems for high-energy savings and new environmentally friendly systems such as solar batteries, fuel cells, hydrogen storage nanotubes and self-cleaning TiO\(_2\) nanomaterials. In addition, the developments of self-assembled nanomaterials to remove hazardous chemical substances selectively, as well as the creations of new nanoporous materials which possess a selective catalytic function, are actively pur-
In oxide nanomaterials, recent progress in nano-fabrication techniques has led to the creation of advanced electronic materials, and various interesting properties have been explored by controlling nanostructures and nanospaces in glasses (amorphous semiconductors), cement constituents (12CaO·7Al2O3) and other commonplace materials. These materials are attracting much attention as key technologies which substitute rare metals and other scarce resources with these abundant elements.

Nanomaterials are also promising as key technologies that will produce breakthroughs in advanced electronic devices. In the semiconductor technologies, increasing density requirements continue to motivate production of microelectronic devices that function reproducibly at ever smaller dimensions (a trend known as Moore’s law). However, current Si-based materials are approaching their physical limit. Continued device scaling will therefore require the replacement of new materials and/or the development of new devices structures such as single-electron devices, molecular devices. At NIMS, we are employing nanomaterial researches targeting for the next generation of DRAM and transistors. Recently, we have succeeded in the development of high-dielectric nanomaterials (titanium oxide nanosheets) that have superior energy-saving characteristics (Fig. 7.3.1). These nanomaterials exhibit both high dielectric constant (> 123) and low leakage current density ($J < 10^{-7}$ A cm$^{-2}$) for thickness down to 5 nm while eliminating problems resulting from the size effect encountered in current devices. In particular, superior energy-saving characteristics of this material is particularly important to this field, and our nanosheet thus provides new opportunities for the development of microelectronics devices that will produce low power consumption to reduce 1 μW per device (roughly 1/100 in current devices). Moreover, this material has an additional advantage in devices fabrications, as it offers the room temperature manufacturing of active devices in the absence of costly fabrication. Such a fabrication technique is critically important to this field, and offers an environmentally friendly process that is not attainable in conventional processes.

4. Future prospects and challenges

The utilization of the superior functions of nanomaterials is expected to contribute to environmental improvement and conservation, as well as environmentally friendly technologies for new energy and energy saving. In the course of practical applications, however, conventional techniques for device fabrications cannot be applied to those new nanomaterials. In addition, nanomaterials behave differently than other similarly-sized particles. It is therefore necessary to develop specialized approaches to testing and monitoring their effects on human health and on the environment. In order to produce true breakthroughs using these nanomaterials, we have to innovate new systems incorporating nanomaterials and conduct system-oriented researches that cover diverse application fields of nanomaterials.

References

1. Basics of the Materials

Recent years have seen active developments in organic electronic devices and among these, the appearance of organic electroluminescent (EL) devices used in displays is still fresh in memory. These may be followed up by organic transistors, organic solar cells and other devices. All of these are actual examples of using organic materials as semiconductor materials. Elemental technologies that typically serve as the basis for semiconductor devices include crystal growth and carrier control. Carrier control may be achieved in conventional semiconductor devices by means of the injection of a dopant into a substrate crystal, but with organic semiconductors, neither these crystal growth or carrier control technologies have been established. In the case of organic crystal growth, the problem of how to get the individual molecules to align when viewed microscopically will probably be the key to the future. As for carrier control, the establishment of dopant technologies and the control of conductivity by means of charge transfer complexes will become essential. On the other hand, research has long been conducted in the area of self-assembly which is a phenomenon peculiar to organic molecules. This makes it possible to appropriately design single molecules (0-dimensional), wires (1-dimensional), molecule films (2-dimensional) and various other assemblies. Thus, research has commenced upon utilizing the self-assembly of molecules to make a new start in order to achieve the aforementioned growth of organic crystals and carrier control.

2. Research trends

Up until now, typical examples of molecular assembly have included the manufacture of single-molecule films (2-dimensional) or molecular wires (1-dimensional). In either case, various types of molecular assembly have been successful due to the self-assembly properties of the molecules. With single-molecule films in particular, much research into the alignment of molecules using scanning tunneling microscopy (STM) has been reported. Conventionally, the assembly of single-molecule components had been the subject of that research, but more recently, research aiming to assemble different types of materials on the atomic and molecular levels has been seen. For example, metal atomic-molecular coordinate bonded assembly, hydrogen-bonded assembly, donor-acceptor pair assembly, organic-inorganic superlattices and others can be cited. As one example, Fig. 7.4.1 presents STM images of the mixed assembly of different types of molecules by alternating alignment of a fluorophthalocyanine which is an n-type organic semiconductor and a perylene derivative which is a p-type organic semiconductor. This becomes a combination of a donor/acceptor pair, so it is highly anticipated as a molecular assembly that achieves both carrier control and crystal growth. When applications to devices are considered, it will be necessary in the future to form a multilayer film where these mixed-type molecular layers are overlaid upon each other.

One other type of device development using molecular assembly is the growth of molecular wires and their application to transistors. By using a semiconductor that is grown in one dimension as the channel layer of a transistor, this is attempting to achieve a high on/off ratio and high density. These are built not with conventional process technologies, but rather experiments aiming to build up nanowires by utilizing the self-assembly properties of molecules have become lively. There have already been many researches on p-type/n-type organic semiconductor wire transistors, and among them, there have also been reports of combining them for applications in CMOS devices.

3. Applications to energy and the environment

The development of organic electronics had previously been concerned with its application to lightweight and thin devices, but more recently, there has been a focus on the environment and energy problems, and accordingly they have attracted attention as eco-materials and alternative materials as substitutes for rare materials. For example, while silicon (Si) is mainly used as the material for solar cells and thin-film transistors, demand for such is expected to increase in the future. At this time, the value of organic materials as an alternative material for Si is also being reviewed. While the conventional amorphous silicon thin films are deposited by plasma CVD processes which consume large amounts of power, they may replaced by organic thin films that could be produced by printing methods or other low-temperature, less energy-intensive processes. In addition, development is pro-
ceeding on the so-called “all organic” devices that use organic materials for all components from the circuit substrate to the electrode materials, semiconductor thin films and even insulator thin films. This has an advantage in that the environmental impact can be reduced in the fabrication process and also in that it uses “disposable” materials that can be easily disposed of after use. If such research into organic electronics proceeds in the future, it may thus be possible to recycle electronic equipment in the same manner as we currently reuse plastic bottles.

4. Challenges in materials science

In order to aim for innovations in organic electronics in the future, it will be necessary to revise both crystal growth and carrier control again. To this end, the necessity is high for establishing assembly technologies where single molecules are stacked up as building blocks. We have pointed out its manufacturing processes which have a low impact on the environment as an advantage of organic electronics, but on the other hand, with only this advantage, it is inconceivable that organic materials will replace conventional semiconductor materials and other solid-state materials without modification. In the future also, wide-spread adoption will be difficult unless both improvements in device performance and process development are achieved. In order to do so, as described above, organic crystal technologies and particularly molecular assembly technologies mixing different types of molecules and carrier control technologies must be improved. Let me present below several problems that must be solved in the field of organic electronics devices.

1) For organic transistors, while research into low-molecular-weight materials as organic transistors is advanced, the development of high-molecular-weight materials is delayed. In particular, commercialization will be difficult unless high-molecular-weight materials with good carrier mobility and techniques for depositing them are established.

2) In the development of organic transistors, the carrier mobility had been used as an index for device development, and as a result, performance comparable to amorphous silicon has been achieved. The next challenge will be the need to reduce the drive voltage. Currently, the threshold voltage for transistor operation is on the order of dozens of volts, but this will need to be reduced by an order of magnitude.

3) For the commercialization of solar cells, a conversion efficiency of 15% or greater is said to be required. However, the conversion efficiencies achieved have been only roughly 11% in dye-sensitized solar cells and roughly 6% in bulk-heterojunction organic solar cells. In bulk-heterojunction organic solar cells in particular, it is necessary to finely align molecules of different types (p-type/n-type) and thus achieve the simultaneous production, separation and transport of carriers from light absorption. To this end, research into the stacking of molecule assemblies on the single molecule level as introduced in this paper is desired.

4) As expected, the control of carriers is necessary for use as a semiconductor material. Up until now, I2 had been used as a dopant in organic materials, but problems remain in regard to its safety in the atmosphere. To solve this problem, it will be necessary to form donor/acceptor pairs by combining p-type/n-type materials, and control their mixing ratios and alignment, and thus establish carrier control methods not seen in solid-state materials.

References


For those wishing to know more about molecular assembly:

7.5 Nanostructure Control Materials

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1. Introduction

The nanostructure control technologies that are useful in improving the performance of energy and environment-related materials may be broadly divided into two types. One is nanopore structure creation technologies used to create structures known as porous structures. The creation of nanopore structures may increase the surface area and thus greatly improve reaction efficiency per unit surface area/unit volume, or the pores may be utilized to adsorb or filter out harmful substances. Another is nanoparticle-dispersal structure creation technologies. These technologies are structure-control methods that cause particles of compounds to be dispersed. The nanostructures thus obtained are used to increase the fracture strength of materials, allow the characteristics of the dispersed particles themselves to be utilized efficiently, and in the utilization of optical effects that utilize the differences in physical properties between the dispersed particles and the dispersal matrix. In addition, with the recent advances in nanotechnology research, various dispersal structure creation technologies have been proposed using dispersal of pores as well as dispersal of particles and not only in regular dispersal but also regular arrangement.

2. Research trends

2.1 Nanopore structure creation technologies

Porous ceramics comprising nanopores connected to each other are widely used as catalyst carriers or filters, and in addition, various manufacturing methods have been commercialized. A widespread technique is the method of manufacture of porous glass that utilizes the phase-separation phenomena of borosilicate glass. Glass that was heat-treated and phase-separated in the phase-separation temperature range is subjected to acid etching treatment to elute the phases with boron oxide as the primary component, thereby obtaining porous silica glass with pores several nanometers in diameter. When the phase-separation treatment and acid etching is performed after being spun into hollow glass fiber, a heat-resistant hollow-yarn membrane of an inorganic oxide is formed. This can be used in practical applications such as in water purification and various filters. These methods can be used to create connected pores of irregular shapes, but it is not possible to obtain regular arrangements of pores with uniform shapes.

Ceramics that contain regularly arranged nanometer-sized pores include anodized alumina. The anodizing technique has been established as an industrial mass-production technology used for the colorization of aluminum sashes and for improving the chemical durability of aluminum. The technique of producing a similar alumina film on a glass surface has also been developed. When formed on a glass surface, a conductive film is formed upon the surface and then a thin film of aluminum is formed and then anodized. The self-assembly process is utilized so a regularly arranged porous structure can be formed without a mask or the like. The diameters of the pores that can be produced extend over a wide range from several nm to 1 μm. By introducing compounds into the pores by the sol-gel method or the electrodeposition method, these can be used as nanomolds. Moreover, by utilizing the difference in solubility between the anodized alumina and the compounds introduced into the pores, it is possible to form arrays of nanorods or nanotubes on a glass surface. Applications are expected in photocatalysts by introducing titanium oxide or in high-density magnetic recording media by introducing magnetic substances. Fig. 7.5.1 is a SEM photograph of a nickel nanocone array produced using a regular array of pores in anodized alumina as a template. Applications to nonreflective films and the like are expected.

The etching method is also being researched as a method of fabricating pore arrays. This is a very stable method that has the precision of photolithography technologies. By cutting regular holes through the fine machining of a glass film deposited by vapor-phase synthesis methods, the world’s first true photonics crystal was produced. The techniques of ablation machining by means of electron beams and high-power excimer laser light, as well as irradiation with emitted-light x-rays and heavy particle ion beams accelerated to high speeds, and removing the irradiation portions by etching are also used.

![Fig. 7.5.1 Nickel nanocone array fabricated using an anodized pore array as a template](Image)

2.2 Nanoparticle-dispersal structure creation technologies

Well-known uniform dispersal methods include methods that utilize the crystallization or phase separation of glass. In crystallization methods, nanosize crystals are precipitated in heat-treated glass to produce translucent crystallized glass. Materials with superior heat resistance and materials with zero thermal expansion have been obtained. Glass is heated to the crystalline nucleus formation temperature range and then heated further to an even higher temperature to form precipitation nuclei and adjust the crystal size. In addition, as a technique for regularly precipitating

Materials Outlook for Energy and Environment
crystals, there are examples of research using crystallized glass produced by laser light illumination-triggered regular crystal precipitation for second harmonic generation. In addition, using a method based on the regular precipitation of crystals on a glass surface, Takahashi et al. systematically produced transparent crystallized glasses with glass formation systems centered on the B₂O₃-GeO₂ system, and precipitated arrays of ferroelectric crystals on the surface of glass to achieve second harmonic generation. With the phase separation method, in the phenomenon of latent phase separation below the liquid-liquid phase separation or liquid phase curve temperature, the phase separation region of the nucleus formation/growth mechanism is utilized where the phase separation precipitated phase becomes liquid drops (Fig. 7.5.2). After heating the temperature above the indicated phase separation boundary called the unsaturation temperature to obtain a uniform melt, the melt is cooled to and kept in the phase separation temperature region to promote phase separation. Finally, the phase-separated melt is quenched to obtain nanoparticle-dispersed glass. Glass that exhibits optical and magnetic anisotropy is also obtained.

Vapor-phase synthesis methods are also used as orientation dispersal technologies. There are also synthesis methods such as the CVD method where raw-material gases are chemically reacted and their reaction products are deposited upon a substrate as well as the sputtering method where ions are made to collide into the same materials as the target substance, thus knocking off the target ions which are again deposited upon a substrate. Nanostructures are formed by utilizing masks and the self-cloning phenomenon to perform repeated deposits after changing the target substance. This method exhibits both good precision and stability.

The induced structure method utilizing a femtosecond laser is also a method that makes oriented dispersion possible. This is a method where femtosecond laser light is squeezed into glass with lenses, thus inducing structural changes in the irradiated portions and creating portions with a high index of refraction. It is possible to create not only points but also lines, or namely optical waveguides. It has superior controllability and convenience. Femtosecond-pulse laser light is known to induce permanent structural changes (induced structures) that participate in ion electron state changes, in addition to the heating effects when the glass is irradiated. Conceivable applications include high-density three-dimensional optical recording, miniature light emission sources and miniature diffraction gratings among others.

3. Future challenges and trends

The various manufacturing methods introduced here each have their own advantages, but one cannot say which one is superior. They are used appropriately depending on the functions and types of the material to be developed. The vapor-phase synthesis method, laser-induced structure method and etching method are suited to the production of regular two-dimensional or three-dimensional dispersions, but their productivity is not very high. The anodizing method is suited to the manufacture of relatively large oriented nanostructures having a regular structure with good productivity. The crystallization method utilizing precipitation phenomena and the phase separation method are also methods with good productivity, but they require more work to achieve the regular dispersal of crystals. In the future, we expect that various nanomanipulation techniques will be developed and applied to obtain the regular arrangement of particles on the nano level. However, when considering industrial production, the most advanced technologies may not necessarily be effective, but rather it will be necessary to handle this with improved-precision versions of technologies that are already developed.

References

Chapter 8. Clean Processing and Materials for That

8.1 Overview

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1. Introduction

Recently, publicity has been given to Process Intensification (PI), which aims for efficiency and cleanliness in manufacturing materials or products with chemical processes or others. The phrase Process Intensification is as yet not clearly defined in Japan, but the phrase may be said to be a design strategy for improving clean process technology, by optimizing the combination of unit processes and improving dramatically the productivity, efficiency, and safety of a device or process, substantially reducing the environmental impact of the entire process. Not only does Process Intensification improve conventional devices and processes, it also aims for significant performance improvement. In order to achieve such targets, development of epoch-making materials which perform main functions in such unit operations as reaction, synthesis, and separation is absolutely necessary. Through the advancement of nanotechnology, many of the seeds for materials which realize PI can be seen.

This chapter focuses on absorbent materials and separating film materials as representative examples of materials used in these clean processes. In addition, manufacturing processes are not directly related, but we want to outline current trends and topics and future issues for exhaust gas catalytic materials from the perspective of targeting gas purification processes and nature-tech materials from the perspective of low environmental impact processes learning from nature.

First, in section 8.2 we outline inorganic based absorbent materials by classifying these materials into 4 categories as layer-shaped absorbents, microporous material, mesoporous material, and macroporous material.

As operations are possible under mild conditions for the separation using membranes, mentioned in section 8.3, it drastically reduces the required energy and to make the design simple, exceptionally low environmental impact is achieved compared to separation and refining by distillation or PSA (Pressure Swing Absorption). Separation membranes provide the key for solving the earth’s environmental problems, such as the separation and recovery of carbon dioxide, in addition to the materials’ role in manufacturing processes.

While referring to the concept of combustion and the strengthening of exhaust gas controls in a trend for exhaust gas catalytic material in section 8.4, we introduce, as an example, a representative ternary catalyst. Not mentioned here, an intelligent catalyst has been developed by Tanaka et al. of Daihatsu Motor Co., Ltd. which is epoch-making achievement as exhaust gas purification catalyst for our country. This catalyst has arrangement of noble metal particles within a crystalline lattice of perovskite-type oxides. The noble metal enters and exits from the crystal (solid solution and precipitation) according to fluctuations in natural oxidation-reduction of exhaust gases. It can maintain a well-dispersed nano level condition and realize a self-reproduction function which can maintain high catalytic activity almost eternally. It also succeeded in a large scale reduction in the amount of noble metal used and at the same time producing a long life span. The catalyst has already been applied in actual use.

Nature-tech materials are described in section 8.5. By viewing, from the perspective of material science, natural cycles which are the result of repeated verification and selection on the earth’s history, we propose completely new approaches to make new products and styles by redesigning the requirements.

2. Keywords from Material Science

In reality, clean processing and materials for that, which are discussed in this chapter, are in a field for which it is difficult to say that a “material science” approach is sufficient. The control of space structures which contain fine holes is quite important for porous materials or membranes. However rarely are attempts made with the objective of dramatic improvements in properties from the control of the microstructure of materials. It is also true for catalysts. It can be said that the field for clean processing and materials so that overflows with dreams of accomplishments in which there remains significant rooms for material science to contribute. In addition, this field is a field where detailed collaboration and exchange are necessary among material science, chemistry, and chemical engineering. Keywords for materials development include surface/interface, low environmental impact, nanotechnology, self-assembly, and structure control.

References

1. Basics of materials

Adsorption refers to a phenomenon in which matter is condensed on the interface of solid/liquid or solid/gas and is classified into physical adsorption and chemical adsorption. Chemical adsorption can be considered to be a chemical reaction between the surface of the adsorbent material and the guest, whereas physical adsorption is recognized one by van der Waals’ forces.

There are many adsorbent materials, such as charcoal and silica gel and so on. These materials have been used in the removal of toxic substances and in various other fields ever since the times of the ancient Egyptians. They have once again regained center stage as important materials for solving the following problems:

- The earth’s environmental problems
- Radioactive waste management
- Global warming problems
- Element strategies.

For water environment problems, ion exchange polymer membranes are being used for the elimination of metal ion or phenol from discharged water and for the purification of sea water. Their contributions to industrial significance should be incalculable.

From the point of view of controlling the amount of carbon dioxide for global warming problems, adsorbent materials are being developed for storing natural gas and hydrogen.

On the other hand, from element strategies perspective, they will play important roles in recycling techniques and as materials for 1) effective and efficient extraction of rare metal elements from mined ores, 2) toxic substance managements and environmental problems from mining resources, and 3) efficient separation and collection of rare metal in discarded industrial problems which have recently been pointed out as “urban mines”.

2. Recent trends

Inorganic adsorbent materials are largely categorized by their structural characteristics into layered and porous substances. Porous substances are subcategorized according to the size of the pore’s diameter; micropore (pore diameter 2nm or less), mesopore (2-50nm), and macropore (50nm or more) (Fig. 8.2.1).

2.1 Layered adsorbent materials and their reconstruction to porous structure

Because layered silicate clay materials, especially smectite, have the ability to react with organic compounds in addition to adsorbent and catalytic characteristics, they have been used for adsorbing, decomposing, and removing toxic substances. Hydroxyapatite, a main component of the tooth and an important biological material, not only undergoes cation exchange reactions, but also takes up coexisting anions at the same time. Therefore it has the characteristics of an adsorption and removal material for both cations and anions. Other well-known useful cation adsorbents are series of layered oxides containing transition metal, e.g., layered titanate. Layered double hydroxide hydrotalcite, on the other hand, is an example of anion adsorbent. When baked, the material becomes mixed oxide, but in water, through the adsorption of anions, the material has once again to hydrotalcite structure. From these characteristics, the material has attracted attention as an outstanding adsorbent for organic dyes which exist in water as anions, and also for being easy to recycle through calcination.

In order to enhance the function of layered adsorbent materials, ceramic particles are used to form pillars between the 2-dimensional layers of clay minerals or layered titanate to create microporous or mesoporous structure. Besides applications as selective adsorbent materials for dioxin etc., it is hoped that these materials will also be used as catalysts in view of their high-specific surface area.

2.2 Microporous materials

Zeolite is a crystalline aluminosilicate with micropores. It has adsorption, separation, and catalysis of gases using physical properties such as its specific pore diameter, ion-exchange capacity and adsorption-separation abilities. Although zeolite has been used, it is recognized again as a new functional material. Up to
date, there are more than 130 types of zeolite with different chemical compositions and crystal structures. In order to improve its adsorption property, it has focused on the syntheses of zeolites having new structures, large pore diameter zeolites which can be used with large sized reactants, and high performance gas adsorbing materials or catalysts which include transition metal complexes in the pores. Furthermore, organic-inorganic hybrid zeolites which incorporate organic functions within the zeolite framework have been synthesized. This material has the same framework structure with known zeolites, but because their surfaces have high hydrophobic/lipophilic properties, it is hoped that this material can be used as an adsorbent for organic matters.

As novel materials for simultaneous removal of cations and anions, composite materials have been developed; that is, zeolites coated on the surface with anion adsorbing layered double hydroxides, or hydroxyapatite coated with nano size. The latter has also been recognized as a long term stable disposal material for radioactive waste (iodine 129 etc.) utilizing apatite’s low solubility property.

2.3 Mesoporous materials

Mesoporous silica has attentions since the first paper published by Prof. Kuroda et al. at the beginning of the 1990s and from the discovery of the MCM41 family by Mobil Corp. These materials are obtained by performing structural control on inorganic substances using surfactants as structural template, and then removing them. Since then, many researchers have been conducted to enhance the control of pore diameter, pore structure (two and three-dimensional hexagonal, cubic and lamellar structures etc.), shape (powder, thin film, and tube etc.), and chemical composition of pore wall (silica, organic silica, metal oxide, metal non-oxide, sulfides, and phosphates etc.), as well as to improve thermal stability. Consequently, mesoporous materials have started to be used as adsorbent and immobilizing materials for bulky molecules that cannot be processed using microporous materials, environmental hormones, peptides, proteins and enzymes.

Mesoporous materials incorporating an organic functional group (ethylene group, phenylene group or others) within their frameworks have received attention for their ability to enhance hydrophobicity, and also for their use as adsorbent materials for organic compounds contained in solutions and organic vapor.

Mesoporous carbon is one of mesoporous materials created using a mesoporous silica material as template. The process is completed in the following way; filling up carbon source inside its pores, carbonization, and then eliminating silica template. Many researchers have performed the fixation of biological polymers, VOC and elimination of harmful organic substances using this material.

2.4 Macroporous materials

Three-dimensional macroporous materials (termed inverted-opal structures) have been synthesized for improving adsorption functions for large molecules. They have obtained by filled up the interfaces of closest packed monodisperse spheres by raw materials. In addition, microporous or macroporous zeolites have synthesized from starting gels containing fine carbon black fine particles with the structural templates. There have been reports of zeolite crystallization that have the hierarchical pore structures by hydrothermal reactions with two-dimensional pore silica gel, with large pores and small pores arranged hierarchically, and structural templates. The method have been attracted for three-dimensional structural control of silica alumina series materials, and also mixed metal oxides series.

3. Future issues

Diverse and complicated global environmental problems must be solved in order to create a healthy, stable, safe and sustainable 21st century society. Adsorbent materials need to enhance selective and effective adsorption of the guest in problems. In order to solve them, their functions must be improved significantly by controlling the materials’ structure at nano-scale. From the perspective of element strategies, adsorption materials must be obtained from ubiquitous elements. From the point of the environment and energy problems, on the other hand, materials can be produced through simple synthesis processes that do not consume too much energy.

References

1. Separation Objectives and Membrane Materials

Separation membrane materials are materials for separating target components by using selective membrane permeation of gases or liquids, etc. For example, reverse osmosis membranes are used in desalination plants to remove the dissolved ions from the seawater under high pressure. Crosslinked polymers such as polyamide or polyimide are used in practical reverse osmosis membranes. The polymer in these membranes has sub-nanometer size pores and has excellent chemical and mechanical characteristics. There are various separation membrane materials to choose from depending on the objective of separation or the required performance. Also, reverse osmosis membranes may have a composite membrane structure formed from a porous membrane (normally polysulphone) that supports the crosslinked polymer and non-woven cloth. As a result it is difficult to classify separation membrane materials as materials. In this section an overview of separation membrane materials is provided according to the purpose of separation.

1.1 Gas separation

There are big expectations that hydrogen will become a source of clean energy as an alternative to oil. Hydrogen is normally produced by steam reforming of hydrocarbons. However, technology is being developed to directly separate hydrogen in reactors using porous ceramic membranes (NEDO high efficiency high temperature hydrogen separation membrane development project). A hydrogen separation membrane having 0.3nm diameter pores in an amorphous silica ceramic membrane, temperature resistant up to 500 °C or higher has been developed, and commercialization is expected in a few years. Separation using metal membranes is effective for producing high purity hydrogen, and research and development on this subject is in progress by Nishimura and others at the National Institute for Materials Science.

Carbon dioxide is larger than hydrogen, but smaller than methane. Carbon dioxide can be separated using a zeolite membrane with appropriate pores. In particular, membrane separation of methane and carbon dioxide is an effective means for purifying natural gas or extracting biogas from the fermentation of raw garbage. Carbon dioxide has a strong affinity for polar organic polymer, and research is being conducted into separation membranes using the difference in partition coefficients. Fluorinated polyimide separation membranes whose carbon dioxide and methane permeabilities differ by more than a factor of 100 and which provide high flux are being developed. The separation membrane method is being investigated for the recovery of large quantities of carbon dioxide emitted from fossil-fueled power station or iron and steel plant, in addition to the absorption method and the adsorption method. The separation membrane method has been reported to be effective in iron and steel plant, which emit carbon dioxide at high concentration.

For oxygen, organic polymer separation membranes are used to provide oxygen enriched air for hospitals or as a component in healthcare products. In particular, the solubility and diffusion coefficient of oxygen in silicone polymer is high, so silicone polymer makes an excellent separation membrane material. Oxygen separation membranes have been researched with the objective of producing high oxygen concentration to improve the combustion efficiency at fossil fueled power stations, etc. In recent years, there has been much research into ceramic oxygen separation membranes in order to supply oxygen at high temperature by oxygen reforming using methane.

Other examples of the practical use of gas separation membranes include the recovery of helium from helium containing gases, and dehumidification for precision instruments, etc.

1.2 Liquid separation

Water is one of the most important natural resources for human beings. Until the 1980s, separation membrane technology was limited to uses in applications for desalination or the production of ultra pure water. However, with the shortage of water throughout the world, the role of separation membrane technology in water processing is expanding in groundwater purification, recycling of sewage and industrial water, the construction of large scale desalination facilities, etc. Reverse osmosis membranes have a composite membrane structure in which a dense layer of crosslinked polymer made by the interfacial polymerization method is formed on the surface of an asymmetric membrane prepared by the Loeb-Sourirajan method. The performance of the reverse osmosis membrane is greatly improved by control of the nano-structure of the dense membrane, although no major change can be seen in the structure itself. The cost of producing 1m³ of fresh water is now about 100 yen.

In Europe and the USA, the demand for nanofiltration membranes for softening groundwater or river water and removing coloring components such as humic acids, etc., is increasing. These membranes have 2nm or smaller pores, which are larger than those of reverse osmosis membranes, and are mostly polyamide composite membranes.

Ethanol is obtained by fermentation of biomass, and it has been
attracting much attention as a new energy source. The concentration of ethanol obtained from bio-fermentation is about 10wt%, and it requires a multi-stage distillation process to refine it. In recent years, there has been much research into refining ethanol by separation membrane technology, using vaporization-permeation methods\(^5\).

2. The search for new membrane materials

The performance of gas separation membranes is determined by the magnitude of the gas permeability, and for reverse osmosis membranes it is evaluated using the water permeation flux and solute rejection coefficient. To achieve a large permeation flow rate is an important index in the search for new membrane materials, regardless of the target component. The flux (\(J\)) is the permeation flow rate per unit area per unit time, and is expressed by the following equation\(^6\):

\[
J = \frac{\text{permeation flow rate}}{\text{membrane area} \times \text{time}}
\]

Also, from the Hagen Poiseuille equation, the flux of a liquid passing through a membrane having pores of radius \(r\) (m) at a density \(\varepsilon (A/A)\) and whose thickness is \(\delta\) (m) is given by the following equation.

\[
J = \frac{(\varepsilon \pi r^2) \Delta p}{8 \mu \delta \tau}
\]

Where \(\Delta p\) is the pressure difference (Pa), \(\mu\) is the viscosity of the liquid (Pa•sec), and \(\tau\) is the tortuosity factor. To increase the permeation flux, it is necessary to increase the pore density of the material, and make the separation membranes thinner. Also, to increase the permeation flow rate, it is necessary to produce membranes with large areas.

By designing the structure, controlling the phase separation structure, and optimizing the thin membrane manufacturing processes of polymer materials and others, the performance of separation membranes can be improved. However, it is not necessarily easy to find materials without problems of manufacturing cost or durability, etc., and whose performance exceeds that of existing products. On the other hand, inorganic membranes have heat resistance and solvent resistance, so it is expected that they can be used in new applications. Various membrane manufacturing methods and pore size control methods have been proposed for zeolite membranes and silica/zirconia membranes, and they are being developed to the stage of practical application\(^3\).

In recent years, it has been experimentally confirmed that water fluxes about 10,000 times higher than the value predicted from fluid dynamics are obtainable with carbon-nanotubes-containing polymer membranes of several \(\mu\)m thick, and this has been the focus of much attention\(^7\). It seems that this phenomenon is due to friction between the inside walls of the nanotubes and the water being so small that it can be ignored. Also, it has been reported that when a silicon porous free-standing membrane of thickness 10nm is used as an ultrafiltration membrane, excellent separation characteristics were obtained (Fig. 8.3.1). Free-standing membranes with controlled nano-structures hold many possibilities as new membrane materials\(^8\).

3. Challenges in materials science

Separation membrane materials are absolutely essential materials for overcoming the energy and environmental problems of the 21st century. However, in some cases the quantities to be processed are enormous, such as the separation of carbon dioxide, etc., so the efforts for this technological revolution are not easy. Also, to solve the water problems of developing countries, limitless low cost water processing technology will be necessary. In the separation membrane research of the future, comprehensive investigations into finding new materials, controlling pores from the nano to the sub-nano level, and optimization by computational science, in addition to material cost, manufacturing cost, and operation cost will be important.

References

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1. Materials development background

Currently, most of the energy consumption in the world is supplied by fossil fuels (oil, coal, and natural gas) with hydrocarbons \((C_xH_y)\) as the principal component. Envisioning the future depletion of fossil fuel stock, “renewable energy source” development is in progress as typified by solar energy generation and wind power generation, but it is expected that the dependence on fossil fuels will continue to grow for at least another 20 years\(^1\).

The chemical energy that is present in fossil fuels is consumed, for the most part, by conversion into electrical or mechanical energy by combustion systems. Representative combustion systems include internal combustion engines found in cars and locomotives and gas turbine system in thermal electric power generation.

Combustion systems are defined as systems which draw out electrical or mechanical energy (work) by causing chemical reactions between fuels and oxidants and converting that to exhausts (Fig. 8.4.1). Using pure hydrocarbons and oxygen respectively as fuels and oxidants, only carbon dioxide \((CO_2)\) and water \((H_2O)\) are discharged as exhausts from combustion systems when theoretical energy efficiency is thermodynamically realized.

Actual combustion systems, generally, use air instead of pure oxygen as an oxidant. In addition to discharging carbon monoxide \((CO)\) and hydrocarbons \((C_xH_y)\) generated by incomplete combustion of the fuels, nitric oxide \((NO)\) generated by the oxidation of nitrogen \((N_2)\) contained in the air is also discharged. CO and NO are gases which are strongly toxic for human. Methane \((CH_4)\) and nitrous oxide \((N_2O)\) which is the principal components of \(C_xH_y\) and \(NO\) respectively are both known to exhibit strong greenhouse effects. Regulations around the world on toxic gases present in combustion systems exhausts have continuously been strengthened over the past several decades (Fig. 8.4.2)\(^2\).

2. Trends in materials development

In order to respond to the exhaust regulations which are becoming stricter each year, “exhaust gas catalyst materials”, which detoxify toxic gas component within the exhaust by converting them to \(CO_2, H_2O,\) or \(N_2\) have been developed since the 1970s mainly in the US. Three-way catalysts (TWC) are representative examples whose principal application is the purification of car exhaust gases.

TWCs are generally complex materials formed by dispersing and loading nano particles of noble metals such as platinum, rhodium or palladium on porous materials composed mainly of oxides such as \(\gamma\)-alumina \((\gamma-Al_2O_3)\), silica \((SiO_2)\) and ceria \((CeO_2)\) (Fig. 8.4.3)\(^2\).
TWC promotes the following three kinds of chemical reactions under normal pressure and in a temperature range of 500 °C or less. Today, TWC has reached the stage where it is capable of simultaneously promoting chemical reactions (1) to (3) at a yield of almost 100% when the mass ratio of the fuel and oxidant is very close to the stoichiometric ratio (in the case of a gasoline engine, 1: 15 ± 1)

\[
\begin{align*}
\text{CO} + \frac{1}{2} \text{O}_2 & \rightarrow \text{CO}_2 \\
\text{C}_x \text{H}_y + (x+y/4) \text{O}_2 & \rightarrow x \text{CO}_2 + y/2 \text{H}_2\text{O} \\
\text{NO}_z & \rightarrow \frac{1}{2} \text{N}_2 + z/2 \text{O}_2
\end{align*}
\]

(1) (2) (3)

Because TWC’s catalytic activity is rapidly reduced when the air-fuel ratio is slightly different from its ideal value, strict control of the air-fuel ratio is a prerequisite for application (Fig. 8.4.4). When the air-fuel ratio is changed following load changes in the combustion system, TWC’s effective catalytic activity is greatly reduced. Currently, new technology is being developed for improving TWC’s effective catalytic activity by adding a 3rd agent such as barium oxide (BaO) which reversibly absorbs and emits NOz and by mitigating the air-fuel ratio changes while the combustion system is active

3. Materials development challenges

Combustion systems that can be operated in lean running conditions are currently being developed with the aim of improving fuel efficiency. However, existing TWCs can not exhibit sufficient exhaust gas cleansing ability in lean running conditions.

There is demand for new exhaust gas catalyst materials that can demonstrate high catalytic activity under air-fuel ratio conditions at variance with the stoichiometric ratio. The following four items are some of the issues that exhaust gas catalyst materials must overcome in the years ahead.

1. Maintenance of catalytic activity when used in high temperature conditions over extended periods
2. Detoxification of CO in lean running conditions
3. Detoxification of NOz in rich running conditions, low temperature conditions
4. Reduction of noble metal contents

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8.5 Nature Tech Materials

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1. Trends in nature-guided materials processing

Learning from, and attempting to come closer to duplicating the wonders of nature has continued to be an age old challenge for researchers and engineers. With the widespread use of measurement and processing tools today due to the advancements in nanotechnology, in many fields, it is becoming increasingly possible to make breakthroughs that come close to the truly complex mechanism of nature rather than simply simulate the pattern as in the past.

If we look at the activities that have taken place in Japan during the last few years, at the vanguard of these trends Nagoya University’s 21st Century COE Program “The Creation of Nature-Guided Materials Processing” and Osaka University’s Program “The Creation of Integrated EcoChemistry” have already completed, and the accomplishments have been distributed across various fields. At Doshisha University “Biomimetics Research Center”, which aims at multidisciplinary research, was established in 2003. The group under Professor Takayuki Nagashima at Tokyo University of Agriculture learns from insects and advocates “Insect Technology” for achieving a sustainable society. Sekisui Chemical Co. Ltd has operated the “Nature-Guided Material Processing Research Fund” since 2002 and receives more than 300 applications every year.

One noteworthy point is, as shown in Fig. 8.5.1, keywords for most of these activities are “Low Environmental Impact” or “Eco” along with “Nano”. While “Nano” is the academic/technical background expressing the level of dimension and tool technology of the research subject, “Eco” represents the social background. This shows that a lot of research has come to recognize the importance of learning from nature and living organisms from the viewpoint of “What is the technology that does not really place a burden on the earth?”

2. Nature Tech

“Nature Tech” was advocated by Tohoku University’s professor Hideki Ishida in 2005. It proposes a completely new approach to manufacturing and lifestyle by scientifically looking at “Nature’s Cycle” which is a product of the endless repetition of verification and selection throughout Earth’s history and by redesigning what are essential for the human ecosystem among them (Fig. 8.5.2). Materials specialists and researchers in fields such as agriculture and mechanical systems participate in the Nature Tech Research Consortium, forming the cross-sectoral type group. The number of participants has been increasing every time a Nature Tech related symposium has been organized by the Japan Institute of Metals and other members. More than 40 lectures were delivered in the Nature Tech session of the MRS Japan Academic Symposium in 2007.

Although the number of people advocating Nature Tech is increasing year by year as more and more people are gaining an understanding of the concept, there is far more research underway that actually fit to the definition of Nature Tech, as one can

3. Nature Tech materials as seen from process perspective

Fig. 8.5.2 Concept of Nature Tech

Fig. 8.5.1 Recent trends in bio (Nature) mimetics

Recent Bio (Nature) Mimetics

Keywords

“NANO”
- Subject of research is “Nano”
- Technology tool is “Nano”

“ENVIRONMENT”
- Growing concerns over environmental problems
- Desire for new technology appearance

Scientific Platform

Nature Technology

Innovative Life Stage

Innovative Manufacturing

Technological Platform

Nature Mimery (Bio-mimicry, Geo-mimicry)

Concept of nature-inspired technology that does not burden the environment
understand from the number of applications received by Sekisui Chemical Co. Ltd. For the purposes of setting out an example, they can be divided into, □ Learning the process of nature, □ Acquiring the functionality by studying the structure and the system, □ Using the material of natural origin or the material that exists naturally. Here, I would like to introduce Nature Tech material giving examples from the viewpoint of environment-friendly material processing or the material technology that is useful in achieving that.

□ Learning the process of nature: Although most of the biotic processes take place at normal temperature and pressure without using or excreting substances that are harmful to biological objects, they are far too complex for human beings to imitate and often unsuitable for industrial high speed mass production. Rather than imitating the entire process, it is more important to extract the essence. For example, self-assembly of tissue, a concept that was derived from the biomineralization of seashells, is expected to be applied in device materials, biomaterial and purification material, etc. The chemosynthesis technology that uses the enzymatic catalytic reaction that takes place within a living organism is also the subject of intense research activity. In addition to living organisms, research is also underway into inorganic material synthesis and solidification molding technologies that simulate the generation process of minerals.

□ Creating from the material of natural origin: There are substances called biomass material and bio-based polymer. In technologies that use natural materials such as chitosan, natural rubber, wood, and silk in their pristine state, research is underway on new methods of using natural materials and developing derivatives. In its broader sense, improved breeding to increase the yield and properties of natural material can be included in Nature Tech. In technologies that synthesize material from raw biological material, polylactic acid synthesized from lactic acid obtained by fermenting cereal grain is already in full commercial production. Work continues to reduce costs and improve resistance to shock and heat. In areas other than “Bio”, humidity regulating materials and adsorption materials are being developed from diatomaceous earth and clay mineral.

□ Material technology that is useful for environment-friendly processing: I will introduce a few material technologies that are useful to environment-friendly processing and new ecosystems. For example, bonding technology in the past did not take into consideration the concept of separation for disposal and presented an obstacle to recycling. However, a new bonding technology is being proposed which is self-separating when required, much like cleavage on a leaf. Humidity and air temperature regulating systems using natural mechanisms are also being developed. These include the use of high adsorption minerals in desiccant air conditioning systems and humidity regulating materials incorporating the mesoporous structure of soil etc (non-powered air conditioning). Maintenance-free soiling preventions systems are available and use the super-hydrophilic or super-hydrophobic properties of the surface structures on the shell and lotus leaves.

4. The future of Nature Tech material

As we anticipate the onset for even graver environmental problems, the activities in Nature Tech materials will become increasingly important. Until now, the concept of “Learning from Nature and Living Things” has been associated with refined simplicity and beauty, or conversely, mind-boggling complexity and detail. However, we need to learn a lot more from that aspect of nature in which moderation is used to obtain essential structures and functions, using only a minimum of non-hazardous natural elements to create objects with a minimum amount of energy. We need to have the sense and observation skills to re-design as well as techniques to imitate so that we can go beyond just admiring nature.

For further details on Nature Tech material kindly refer to the following:
1) T. Yasuda, T. Kariya, I. Ishida: Atarashi Kurashi No Ka • Ta • Chi (New Lifestyle), Geiritsu Publishing (2007).
2) Abstracts of 18th Japan MRS Academic Symposium, MRS Japan (2007).
1. Introduction

Environmental and energy materials can be classified into three types, structural materials for power generating equipment, functional materials for electronic devices, and new materials of nanomaterials typically. Structural materials, such as those used in power generation plants and aircraft, usually incur large losses when damage occurred and are not easily replaceable. Therefore, diagnosis and lifetime prediction technologies are needed to ensure economic efficiency and reliability. On the other hand, functional materials which allow for easy replacement of parts (commercial products in particular) need to offer reliability in performance and functions over a set period under specified environments. Tables 9.1.1 summarize a phenomena that control the lifetime of environmental and energy materials under consideration in NIMS Outlook, methods for measuring and diagnosing the phenomena and for assessing lifetime.

Degradation factors controlling the lifetime of materials consist of electrical, chemical and mechanical factors; which of these becomes the main factor for determining lifetime depends on the purpose and environment under operation of material.

Table 9.1.1 Phenomena that control the lifetime of the environmental and energy materials, methods for measuring and diagnosing the phenomena and methods for assessing lifetime

<table>
<thead>
<tr>
<th>Item</th>
<th>Material</th>
<th>Phenomenon controlling lifetime</th>
<th>Measurement and diagnosis method</th>
<th>Lifetime assessment method</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic energy material</td>
<td>Ultra supercritical pressure coal fired power generation material</td>
<td>Creep, Fatigue, high-tempereature oxidation/corrosion test, microstructure observations and embrittlement</td>
<td>Creep/Fatigue test, high-temperature oxidation/corrosion test, microstructure observations</td>
<td>Creep/Fatigue test, high-temperature oxidation/corrosion test, microstructure observations</td>
<td>Various evaluation methods have been standardized</td>
</tr>
<tr>
<td>Chemical energy material</td>
<td>Superconducting material</td>
<td>Fatigue, friction (aggressive, chemical, fatigue), creep, heat history, stress from electromagnetism</td>
<td>Superconductivity transition temperature, critical current density, residual strain after heat-cycle test, data friction test, fatigue limit, creep rate</td>
<td>Superconductivity transition temperature, critical current density, residual strain after heat-cycle test, data friction test, fatigue limit, creep rate</td>
<td>Under development</td>
</tr>
<tr>
<td>Energy transportation and transformation material</td>
<td>Magnetic, supermagnetic material</td>
<td>Fatigue, friction, oxidation/corrosion, and creep, heat history, stress from electromagnetism</td>
<td>Superconductivity transition temperature, critical current density, residual strain after heat-cycle test, data friction test, fatigue limit, creep rate</td>
<td>Superconductivity transition temperature, critical current density, residual strain after heat-cycle test, data friction test, fatigue limit, creep rate</td>
<td>Under development</td>
</tr>
<tr>
<td>Nano-driven energy and the environment material</td>
<td>Mechanical property material</td>
<td>Depth and amount of scratches on glass substrate</td>
<td>Measurement of depth and amount of scratches using microscopes, determination in electromagnetic characteristics</td>
<td>Measurement of depth and amount of scratches using microscopes, determination in electromagnetic characteristics</td>
<td>Nothing in particular</td>
</tr>
<tr>
<td>Materials used in clean processing</td>
<td>Nonferrous material</td>
<td>Chemical change, fatigue, abrasion, corrosion, accumulation of microscopic damage, ultraviolet degradation</td>
<td>Various analysis methods, various nondestructive inspection techniques (ultrasound, magnetic, permeation, vortex flow, etc.)</td>
<td>Various analysis methods, various nondestructive inspection techniques (ultrasound, magnetic, permeation, vortex flow, etc.)</td>
<td>Various exposure tests</td>
</tr>
</tbody>
</table>
9.2 Crack Growth and Life Assessment Techniques

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1. Types and characteristics of crack growth

The morphologies and mechanisms of fracture of materials change variously depending on a combination of the loading condition, temperature, environment, etc. Representative examples are brittle fracture (low temperature embrittlement, hydrogen embrittlement), fatigue fracture, creep fracture and corrosion fracture (stress corrosion cracking, corrosion fatigue). Under cyclic stress condition, micro-cracks will initiate in slip bands or non-metallic inclusions, and grow until final fracture (fatigue crack growth). The most characteristic phenomenon in fatigue crack growth is the striped pattern called striations, which is the vestige of the fatigue crack growth per 1 cycle of cyclic stress. Under a constant loading condition at high temperature, creep deformation increases with time, and then cracks initiate and grow with time until final fracture. The most distinguished phenomenon in creep fracture is void-type intergranular fracture, in which micro-voids formed at the grain boundaries grow with time and coalesce to form a macro-crack. This phenomenon is often observed for low stress and long-term loading conditions at high temperatures. Stress corrosion cracking (SCC) is a phenomenon, in which cracks initiate and grow with time until brittle final fracture, when tensile stress or tensile residual stress acts under a specific corrosion environment.

2. Diagnosis and life prediction of crack growth

The fracture of materials is a complicated phenomenon related to micro and macro factors. A good deal of research has been conducted about the criterion of initiation and growth of cracks, the dominant fracture mechanics parameters and the life prediction method in structural components, but elucidations are still required in many aspects.

Theoretical research on fractures began with Griffith’s theory (1920), which solved the fracture strength of perfectly elastic bodies containing cracks from the energy equilibrium conditions. After that, it was expanded by Irwin and Orowan to the elastic bodies accompanied by small-scale plastic deformation at the crack tip. Moreover, the stress intensity factor \( K \) was defined as the parameter expressing the stress-strain field in the vicinity of the crack tip when small-scale yielding conditions are satisfied (1957). In addition, the fracture criterion based on the energy release rate was also defined, and after that linear fracture mechanics advanced. There are many cases where the fracture properties of the materials are evaluated based on \( K \), in the case of brittle fracture, fatigue crack growth and crack growth of stress corrosion cracking. On the other hand, the \( J \) integral was proposed by Rice as the criterion for fractures in which large-scale plastic deformation occurs at the crack tip (1968), and nonlinear fracture mechanics progressed. In addition, the \( C^* \) parameter (modified \( J \) integral), which expands the \( J \) integral to creep cracks, was proposed.

The fatigue crack grow rate is generally evaluated by the Paris rule:

\[
\frac{da}{dN} = C (\Delta K)^m
\]  

where, \( \Delta K \) is the stress intensity factor range. In addition, \( \Delta K_{	ext{eff}} \) is commonly used as the effective stress intensity factor range that takes into consideration the fatigue crack closure. The cyclic \( J \) integral \( \Delta J \) is applied to such cases as high temperature low cycle fatigue accompanied by large plastic deformation.

The creep crack growth rate is generally assessed by the following equation:

\[
\frac{da}{dt} = D (C^*)^{m}
\]  

Crack growth life can be calculated by integrating these relations.

3. Evaluation of crack growth at high temperatures

Improving the energy efficiency for high temperature components such as thermal power plants and jet engines is one of the most important issues for energy saving or reducing greenhouse gases. Owing to this, the temperature and loading conditions of high temperature components tend to become more severe for the structural materials. In addition, it is planned to use high temperature plants beyond their design life for economic reasons. Under such circumstances, higher precision of lifetime assessment techniques in high temperature structural components has become a more important research topic.

In the case of turbine rotors and boilers, creep voids form, grow and coalesce to form a micro and macro crack with time during services under high temperature and stress condition. This time dependent crack growth under high temperature and stress condition is called creep crack growth. Researches that apply fracture mechanics to creep crack growth began in the 1970s. Researches were conducted about the fracture mechanics parameters controlling the stress-strain field of the creep crack tip, using various kinds of specimens containing notches or cracks (CT, CCT, SEN, DEN, etc.). Currently, the creep crack growth rate under large-scale creep conditions is being assessed by the above-described equation (2). In addition, international joint research
relating to the measurement and evaluation techniques for creep crack growth is being conducted as one theme in the VAMAS international standardization research project for advanced materials, and the international standard ISO TTA5: 2007(E) and ASTM E1457 for creep crack growth test have been prepared. Currently, research is being actively conducted for applying the \( C^* \) parameter to life prediction of the high temperature structural components.

The ductility of materials, the mechanical constraint at the crack tip (multiaxial stress state), the damage zone formed at the crack tip, etc. affect the creep crack growth rate. Fig. 9.2.1 shows the test results for the effect of specimen size on creep crack growth rate \( (da/dt) \) versus \( C^* \) relations using large CT specimens for 1Cr-Mo-V turbine rotor steel. It can be seen that, the crack growth rate of the thick specimens \((B = 63.5 \text{ mm}, ~\square\) in the figure) is approximately 5 times faster than that of the thin specimens \((B = 6.35 \text{ mm}, ~\square\) in the figure) for the same \( C^* \) value. In addition, the crack growth rate becomes faster by adding a side groove (S.G.). This can be attributed to the fact that creep rupture ductility decreases under the multiaxial stress state. When the thickness of the specimen is increased, the deformation of the crack tip is mechanically constrained and it causes a multiaxial stress state, so the rupture ductility decreases and the crack growth rate is accelerated. In structural components with large thickness, because the stress multiaxiality inside the plate thickness is higher than that at the surface, creep voids or cracks form preferentially inside the plate thickness.

In the advanced high efficiency thermal power plants (ultrasupercritical power plants), high Cr heat resistant steel (9-12% Cr steel) that has a tempered martensite structure has been employed, and its application to the next generation nuclear power plants (fast breeder reactor, high temperature gas cooled reactor) is being examined. When high Cr heat resistant steel is used for long time at 600 °C and above, the decrease of creep life due to a creep crack called Type IV crack, which forms in the heat affected zone (HAZ) of weldment (Fig. 9.2.2), becomes a problem. Since the HAZ that contacts the fused weld metal during welding is rapidly heated to the transformation temperature and rapidly cooled, the martensite structures collapse, and the creep strength decreases. In the weldment, a narrow HAZ with low creep strength is sandwiched between weld metal and base metal with high creep strength, and high multiaxial stress operates on the HAZ due to the mechanical constraint. Because the growth of creep voids and cracks are accelerated and creep ductility decreases under multiaxial stress condition, brittle creep fracture occurs inside the plate thickness (Figure 9.2.2.). Life prediction techniques, nondestructive detection techniques of damages, repair welding techniques and prevention techniques of damages in welded components have become key research issues in order to ensure increased efficiency and safety in power plants.

References

5) F. Abe et al., Creep Resistant Steels, Woodhead Publishing (2008).
1. Basics of fatigue

Research on fatigue boasts a lengthy history of over 120 years, and has achieved remarkable progress during that time. However, even today there appears to be no end to accidents due to fatigue breaking. This means that since the number of factors exerting an effect on fatigue properties is huge, a long period of time will be needed to elucidate the full picture. In addition, new issues are also arising owing to the appearance of new materials and changes in the use environment. Owing to this, research on fatigue can rightly be called basic research that must be continued semipermanently.

The basic mechanism of fatigue is that fine cracks are initiated and grow due to the repetition of a load until this results in fracture. Macro structural changes such as sub-grain formation occur in those cases where large plastic deformation like low cycle fatigue occurs, but no macro structural changes occur in cases of high cycle fatigue, wherein only minor plastic deformation occurs. In addition, high susceptibility to defects is another characteristic of fatigue. Even in the case of minute defects that do not become a problem in static tensile tests, there are cases where they do become a problem in terms of fatigue.

There are many factors that affect the fatigue properties of metal materials, such as the metallurgical factors, the shape dimension factors, the use environment conditions, and so on. Here, I will focus on the key points of the metallurgical factors in order to keep the discussion from being overly discursive. That is, I will provide an account of the standard fatigue properties of metal materials in a room temperature atmosphere.

2. Assessment of fatigue strength

Classifying broadly the metallurgical factors that affect the fatigue properties, these can be divided into structure and static strength. Of course, these two are interrelated, but more systematic organization is enabled by focusing on the static strength when assessing the fatigue strength. For example, the fatigue limit \(\sigma_w\) of steel materials stands in the following relationship to the tensile strength \(\sigma_B\) and Vickers hardness \(H_V\).

\[
\sigma_w = 0.5\sigma_B = 1.6H_V
\]  
(1)

Here, the fatigue limit refers to the stress of the limit at which fatigue break does not occur even when it is repeated an infinite number of cycles, and ordinarily this can be determined with a fatigue test up to \(10^7\) cycles. In addition, since not only the fatigue limit but also the finite life strength (the fatigue strength relative to a certain number of repetitions) exhibits the same relationship as equation (1), by standardizing the vertical axis (stress amplitude) of an \(S-N\) diagram with the tensile strength or Vickers hardness, it is possible to summarize the \(S-N\) curve of multiple materials with different static strengths in one curve. Such a standardized \(S-N\) curve can be employed for estimating the finite life strength or fatigue life.

The relationship in equation (1) is established when absolutely no defects are present, but it becomes the following sort of relationship when minute defects are present on the surface of the materials.

\[
\sigma_w = 1.43 \left( \frac{H_V + 120}{\sqrt{\text{area}}} \right)^{1/6}
\]  
(2)

Where, the \(\sqrt{\text{area}}\) (\(\mu\)m) is the square root of the projected area of the defect in the axial direction. The factor 1.43 for the numerator becomes 1.56 in the event that defects are present inside the material.

The above relates to materials that exhibit a fatigue limit. On the other hand, many materials that do not exhibit a fatigue limit are present in metal materials. For example, the fatigue limit disappears in the case of high strength steels even though steel materials ordinarily exhibit a fatigue limit. Figure 9.3.1 shows the relationship between the tensile strength and fatigue strength of steel materials, but equation (1) has overestimated the fatigue strength owing to the disappearance of the fatigue limit in the case of steel whose tensile strength is 1,200 MPa and above. This phenomenon is called gigacycle fatigue, and in recent years it has been researched actively.

Fig. 9.3.2 shows a typical \(S-N\) curve for high strength steel. In ordinary fatigue a surface fracture in which the cracks are initiated from the surface of the test piece occurs, but in the long life region an internal fracture whose starting point is an inclusion or
others occurs. Therefore, the estimation of internal fatigue strength becomes important in the assessment of gigacycle fatigue. Even in the case of gigacycle fatigue, it is reported that this can be estimated by equation (2) (the factor is 1.56) provided that it is a finite life strength at $10^7$ cycles. Moreover, there is a theory that holds that it is also possible to estimate a finite life strength at more than $10^7$ cycles by taking into consideration the ODA (optically dark area). However, since the fatigue test data is quantitatively insufficient, no clear conclusion has been obtained yet. The cause of the shortage of data is the fact that a long time from several months to several years is required for the fatigue tests up to gigacycle region. Compared to this, it has become clear from recent research that an ultrasonic fatigue test that can realize a frequency of 20 kHz, which is at least 200 times faster than usual, is effective in assessment of internal fatigue properties. Owing to this discovery, it is anticipated that gigacycle fatigue research will accelerate.

Although internal fractures whose starting point is chiefly inclusions occur in the case of high strength steel, internal fractures whose starting point is the matrix itself (facet) occur in the case of titanium alloy. In this manner, internal fractures are closely related to the microstructure of the materials. In other words, there was little room for incorporating materials science in the case of ordinary surface fractures since it can be organized by just the static strength as in equation (1), but it was just the right time for materials science in the case of internal fractures. Now there are efforts to make full use of materials science to elucidate the internal fracture mechanism, to clarify the distinction between materials that exhibit a fatigue limit and those that do not, and to establish everything up to a method for estimating gigacycle fatigue strength.

3. Diagnosis of fatigue and remaining life assessment

Fatigue occurs due to the initiation and growth of cracks, and almost no macro plastic deformation or structural changes occur in the case of high cycle fatigue. Owing to this, it is hard to grasp the signs, and it frequently becomes the cause of disruptive accidents.

At present, there is no means other than examining whether or not there are cracks as a method for diagnosing the extent of fatigue damage to materials. Methods for examining cracks include dye penetrant testing, magnetic particle testing and ultrasonic testing. Immediate replacement is done at the stage where cracks are found in the case of small components on which a high frequency repeated load acts, but they can be used as is after a remaining life assessment is conducted in the cases of large components on which only a low frequency load acts. The results of a fatigue crack propagation test are required in order to carry out a remaining lifetime assessment. Based on the results of the fatigue crack propagation test, the number of repetitions required for a crack to grow until it is a size where the component breaks is estimated. Such a remaining lifetime assessment becomes necessary when determining the inspection intervals. In other words, it is necessary to set the inspection intervals shorter than the period in which a crack with a size that is just barely within the detection limit grows to a size where it causes the component to break.

In addition, recently research that attempts to grasp the changes in the dislocation structure at the previous stage that grows into cracks by utilizing electromagnetic ultrasound measurements is also being conducted. It has already been reported that there are successful examples of grasping sub-grain formation in the vicinity of the fracture starting point under conditions where the life is relatively short. In this manner, we have reached the stage of introducing materials science in the diagnosis of fatigue and remaining life assessment as well.

References

7) www-ndc.me.es.osaka-u.ac.jp/ogi/fatigue.htm
9.4 Assessment of Creep and Life Prediction Techniques

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1. Significance of creep life prediction

It is possible to achieve higher performance such as improving energy efficiency by raising the operating temperature of high temperature equipment such as thermal and nuclear power generation or engines for transport equipment. However, increasing temperature makes the operating condition of materials more severe, and degradation of material property is promoted and moreover the life of components is also declined. Owing to this, the structural components of boilers and pressure vessels are being designed and manufactured based on the allowable stress regulated in codes and standards, and their safety is assured. In the field of non-nuclear energy, the allowable stress in the high temperature region, where creep deformation becomes a problem, is generally determined by the lowest of the following.\(^1\)

1) 100% of the average stress to produce a creep rate of 0.01%/1,000 hr.
2) 67% of the average stress to cause rupture at the end of 100,000 hr.
3) 80% of the minimum stress to cause rupture at the end of 100,000 hr.

In many cases the stress to cause rupture at the end of 100,000 hours of 2) or 3) determines the allowable stress. Therefore, it is crucial to assess with good precision the stress to cause rupture at the end of 100,000 hours in order to regulate a highly reliable allowable stress.

2. Long-term creep life prediction techniques

2.1 Creep rupture strength

There are two methods for predicting long-term creep strength based on the creep rupture life, the direct method\(^2\) and the time-temperature parameter (TTP) method.\(^3\) The direct method evaluates the relation between the creep rupture time \(t_R\) and stress \(\sigma\) according to equation (1), and calculates the stress to cause rupture at a prescribed time.

\[
\log t_R = a_0 + a_1 \log \sigma + a_2 (\log \sigma)^2 + \ldots + a_k (\log \sigma)^k
\]  

(1)

Here, \(a_0, a_1, a_2, \ldots a_k\) are constants. The direct method extrapolates short time data to long times, and this requires a lot of creep rupture data at the same test temperature as the long time creep strength that one wants to predict. In addition, there is also the problem that it is not possible to predict a decline in strength that originates in degradation of material property that arises during long-term exposure at the elevated temperatures.

On the other hand, TTP method is based on the concept that the creep life as shown in equation (2) is expressed as only a function of the stress, on the assumption that the TTP method compensates for the difference in temperature with the time-temperature parameter \(P\) \((t_R, T)\), and long-term creep rupture life at low temperature is predicted and assessed based on the high temperature, short-term test data.

\[
P (t_R, T) = F (\sigma)
\]  

(2)

The TTP method is useful compared to the above-mentioned direct method, and it has been used widely as an extrapolation method for the long-term creep life. A detailed interpretation of long-term creep life prediction by the TTP method was reported by Fujita, et al.\(^3\) Many kinds of approaches have been proposed for the time-temperature parameter of the TTP method, but the representative ones are shown below.

\[
\text{Larson-Miller: } P = T (\log t_R + C)
\]  

(3)

\[
\text{Orr-Sherby-Dorn: } P = \log t_R - Q / (2.3 RT)
\]  

(4)

\[
\text{Manson-Succop: } P = \log t_R + B \times T
\]  

(5)

\[
\text{Manson-Haferd: } P = (\log t_R - \log t_s) / (T - T_s)
\]  

(6)

where, \(T\) is the absolute temperature, \(t_R\) is the creep rupture time, \(Q\) is the activation energy of creep, \(R\) is the gas constant, and \(C, B, t_s, T_s\) are all constants. The Larson-Miller parameter (3) equation is equivalent to the tempering parameter, and it is most widely used for prediction and assessment of the long-term creep life.

2.2 Creep deformation properties

The creep rate varies from hour to hour, in response to the change in creep strength caused by the changes in microstructure during creep deformation. Particularly in the event that the longterm creep strength is assessed, it is important to consider the effects of degradation of material property due to changes in microstructure. Consequently, the effects of microstructural change that control the creep strength can be understood in detail when the creep deformation behavior itself is analyzed than a case where only the creep rupture is analyzed. Accordingly, the creep curve (strain-time relationship) itself, rather than the time-temperature parameter with which only the creep rupture time is analyzed, is expressed by an equation and the creep deformation behavior is analyzed, and an examination for predicting and assessing long-term creep strength properties has been carried out. In this manner a large number of creep deformation models have been proposed. While the majority of these creep deformation equations are empirical one, there are equations that take into account the macrostructural changes and deformation mecha-
nism. The physical meaning of such models is clear, but they are complicated compared to other empirical equations, and it is also difficult to determine the parameters. These creep constitutive equations provide useful creep deformation properties for the remaining life assessment of components based on the analysis of temperature/stress calculations, and future advances are desired.

3. Higher precision of life prediction techniques

With the high strength ferritit creep resistant steel that has been developed in recently, the steam temperature of the thermal power plants was raised from the previous level of approximately 566 °C. to approximately 600 °C, and this contributed greatly to the improvement of energy efficiency. However, overestimation of the long-term creep strength has been concerned, and a reassessment of the creep strength was conducted after the accident occurred on a hot reheat piping in the operating modern thermal power plant. Fig. 9.4.1 shows the results of the prediction of creep life for KA-SUS410J3 type steels by the conventional method and the region splitting analysis method. In the conventional method, where all the data are analyzed, accuracy of creep life prediction is poor and it tends to overestimate with increase in creep rupture life. Compared to this, the region splitting analysis method can predict with good accuracy the creep rupture life. Since 1/2 of the 0.2% offset yield stress, which is the boundary condition of region splitting, corresponds to the initiation of plastic deformation during high temperature tensile test, namely the proportional limit, it may be useful to assess separately the creep strengths above and below 1/2 of the 0.2% offset yield stress.

4. Future Challenges

As shown by examples of high strength ferrite creep resistant steel, it is not possible to assess fully the strength properties of newly developed materials or age-related degradation behavior merely by an extension of existing technologies. In particular, since phenomena related to materials reliability is strongly dependent on the time, it is not possible to response rapidly by starting an examination once a problem has come to light. When applying newly developed technologies to actual equipments, it is important to undertake an examination of the materials reliability beforehand, and to accumulate knowledge by foreseeing the occurrence of damage, etc. that may occur, before problems arise in actual equipments.

References

9.5 The Assessment of Corrosion, Stress Corrosion Cracking (SCC) and Lifetime Assessment Techniques

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1. Classification and characteristics

The corrosion of metals is classified into two main types depending on whether or not water is involved: wet corrosion and dry corrosion. Atmospheric corrosion is also classified as wet corrosion corresponding to the case where the film of water on the metal is very thin. Dry corrosion becomes a problem in hot environments; at room temperature the speed of corrosion is extremely slow and it does not become an issue. Corrosion generally is the result of chemical reactions, but it can also involve microbes, as in the case of microbiologically induced corrosion. Stress Corrosion Cracking (SCC) can occur under specific conditions when metal corrodes while under stress. The mechanisms of SCC are hydrogen embrittlement, active dissolution and oxide film cracking.

2. Methods of diagnosis

In wet corrosion, it is possible to predict whether the metal will corrode or not, based on equilibrium theory. A consideration of the equilibrium of wet corrosion is made using a Pourbaix voltage-pH diagram that maps out the stable (equilibrium) phases of a thin-film aqueous solution reaction in a specific potential and pH condition. Fig. 9.5.1 shows an example of a Pourbaix diagram of iron, when the concentration of ferrous ions in solution is $10^{-6}$ mol/l. The map shows the various thermodynamically stable electrode voltage-pH areas of metallic iron (Fe), ferrous ions ($Fe^{2+}$, $Fe^{3+}$, …) and ferrous oxides ($Fe_2O_3$, $Fe_3O_4$).

The method used to derive the map boundary lines depends on whether or not electrons participate in the reaction. If electrons do not participate in the reaction:

$$E = E_0 + \frac{RT}{nF} \ln \left( \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \right)$$

For example, for the reaction shown on the diagram, the equation would be:

$$2Fe^{3+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 2e^-$$

The equilibrium conditions for this reaction are:

$$E = E_0 + \frac{RT}{nF} \ln \left( \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}} \right)$$

$$E = 0.73 - 0.177pH - 0.0595 \log (a_{Fe^{2+}})$$

If electrons do not participate in the reaction:

$$M^{n+} + nOH^- \rightarrow M(OH)_n$$

$$\text{pH} = -\frac{1}{n} \log(k) - \log(a_{M^{n+}}) - 14$$

The boundary lines of the area marked out in thick lines in Fig. 9.5.1. are derived from equations (2) and (7). The areas on the map where the ions are stable are the areas where corrosion will occur. The areas where the metal is stable is the area where corrosion will not occur, and the areas where oxides or hydroxides are stable are areas where corrosion is suppressed. In Fig. 9.5.1 the area of actual corrosion is shaded in color, and we can see that it matches well with the area predicted by the electrode electric potential-pH map.

The occurrence of SCC can not be predicted theoretically; the conditions under which cracking will occur must be determined through experimental testing. Various tests are used, including constant load tests, U-bend tests, U-bend with gap test, 3-point bending tests and slow strain-rate tests. However, the test method that the author has recently developed in which a thin sheet of metal is bent with attaching small MgCl$_2$ droplets is simple and highly reproducible. Not only can the load stress be controlled by the radius of curvature of the test piece, but cracks can be made to appear in a short time.

3. Methods for lifetime assessment

In wet corrosion, the lifetime can be predicted by chemical
kinetics. The corrosion reaction of iron in an acid aqueous environment (anodic reaction) is

\[ \text{Fe} = \text{Fe}^{2+} + 2e^- \]  
(8)

For this reaction to proceed, a cathodic reaction has to simultaneously occur to consume the electrons (e\(^-\)) that are generated in equation (8) above. The iron cathodic reaction that occurs in an acidic aqueous environment is:

\[ 2\text{H}^+ + 2e^- = \text{H}_2 \]  
(9)

The hydrogen ions in the solution combine with the electrons to form hydrogen. The electrode potential dependencies of the reaction speeds (current densities) of both reactions are shown in Fig. 9.5.2. The reactions of equations (8) and (9) are expressed as straight lines on the logarithmic axis. Point E, where the two lines intersect (the point where the currents at the anode and cathode are equal) indicates the corrosion potential \( E_{\text{corr}} \) and the corrosion current density \( i_{\text{corr}} \). Nevertheless, both are internal polarization curves and cannot be measured directly. Using an external power source, the electric potential-current curves can be estimated (shown as thick lines in Fig. 9.5.2) when polarized. As shown in the diagram, if the measured current-electric potential curve is separated from \( E_{\text{corr}} \) by more than a certain amount, it will overlap the internal polarization curves, and \( i_{\text{corr}} \) can be estimated by extrapolating the straight part of the curve to point E. This method is called the Tafel extrapolation method. The corrosion speed \( \frac{dh}{dt} \) is expressed by the following equation from the Faraday conversion equation.

\[ \frac{dh}{dt} = \frac{i_{\text{corr}} M}{zF \rho} \]  
(10)

Where, \( M \) is the atomic weight of the metal, \( z \) is the reaction valency, \( F \) is the Faraday constant (96500 C) and \( \rho \) is the density.

On the other hand, when iron is in a neutral aqueous environment that contains dissolved oxygen, instead of the hydrogen generation reaction of Equation (9) consuming the electrons (e\(^-\)) that are produced on the right side of Equation (8), the dissolved oxygen takes up the electrons in a cathodic reduction reaction:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- = 4\text{OH}^- \]  
(11)

The reaction in Equation (11) is a reduction reaction, and if the reaction speed is above a certain level, the diffusion of the oxygen molecules from the solution to the surface of the metal becomes reaction rate-determining and the reaction speed reaches saturation. This saturated reaction speed (current density) is called the dissolved oxygen diffusion limit current density \( i_{\text{LO}} \), and is expressed by the following equation:

\[ i_{\text{LO}} = \frac{zF D_{\text{O}_2} C_{\text{O}_2}}{d} \]  
(12)

Where \( z \) is the number of charges, \( F \) is the Faraday constant, \( D_{\text{O}_2} \) is the dissolved oxygen diffusion constant, \( C_{\text{O}_2} \) is the dissolved oxygen concentration in solution, and \( d \) is the diffusion layer thickness. The intersection of the polarized curve of the anodic reaction in Equation (8) and the cathodic reaction of Equation (10) gives the corrosion potential and the corrosion current density of the system. In other words, in this instance the corrosion speed is mostly governed by the dissolved oxygen cathodic reduction reaction and is not influenced by the anodic reaction. As shown by Equation (12), \( i_{\text{LO}} \) is proportional to the concentration of dissolved oxygen in solution, therefore, as the concentration of dissolved oxygen changes, so does \( i_{\text{LO}} \), and the corrosion speed changes in proportion to the concentration of dissolved oxygen in solution. Moreover, the diffusion layer thickness in Equation (12) is dependent upon the flow velocity; the higher the rate, the faster the corrosion speed.

When the polarization curves cannot be measured, as in the case of atmospheric corrosion, the corrosion speed can be estimated from the change in weight due to atmospheric exposure, the thickness of the oxidation layer and the AC current impedance method. In SCC, while there is no accurate method to estimate service lifetime, researchers have attempted to express it in terms of the propagation speed of cracking (K value). However, since the branching and inclination of crack occurs in SCC, which is unlikely in fatigue cracks, estimation of the K value is difficult.

References


An excellent reference book:

1. Various evaluation methods

Almost all the methods which non-destructively evaluate material structure, mechanical properties, electromagnetic characteristics, strains, and residual stress, can be non-destructive evaluation techniques of materials degradation or damage by studying the relationship between measured parameters and degree of degradation/damage. Although there are many different evaluation methods, due to the principles of each measurement method, there are limitations to the materials to which they can be applied, the environments in which they can be used, and their accuracy and sensitivity. Table 9.6.1 shows some typical non-destructive evaluation methods, the materials they are applied to, their principle and the information that can be gained through their use. The main methods used include ultrasonic waves, electromagnetism and radiation.

Ultrasonic method is the most well-known method to evaluate the state of degradation and damage. Pulse echo method is a technique for evaluating the shape of the defect and its size and location by directing a pulse wave into the material and receiving the echo reflected back from cracks or contaminants. The velocity of the ultrasonic wave $v$ (propagation velocity) can be calculated by the equation:

$$v = \alpha \sqrt{\frac{C_m}{\rho}} \beta \frac{\sigma}{C} \gamma \varepsilon,$$

(1)

Where $C_m$ is the elastic constant, $\rho$ is the density, $\sigma$ is the stress, $\varepsilon$ is the plastic deformation, and $(x)$ is the convolution integral. It follows that when the influence of stress and strain are small, the elastic constant of the material can be evaluated from the density of the material and the propagation velocity of the ultrasonic wave. The elastic constant is a specific value that depends on the composition and structure of the material. From the change in the elastic constant, it is possible to detect the existence of fine cracks, pores and other defects, as well as any changes to the material composition. As can be understood from terms 2 and 3 of Equation (1), the size of the residual stress and plastic deformation can be assessed from the propagation velocity of the ultrasonic wave. Moreover, the attenuation and absorption of the wave and the characteristics of its dispersion are also very useful in the assessment of material degradation and damage. The degree of attenuation $\alpha$ is a function of the frequency $f$ and is expressed by the following equation:

$$\alpha = Af + Bf^2 + Cf^4,$$

(2)

Where $A$, $B$, and $C$ are the constants associated with the hysteresis, damping and thermal conductivity, and the Rayleigh dispersion, respectively, and are closely related to features within the material, such as the dislocation density and crystal interfaces. This all means that the characteristics of a material and its state of degradation can be evaluated from the nature of the frequency dependency of the ultrasonic wave attenuation.

<table>
<thead>
<tr>
<th>NDT Method</th>
<th>Materials</th>
<th>Physical principles</th>
<th>Detectable phenomena</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrasonic</td>
<td>Metals, Ceramics, Plastics, Composites, Concrete, etc.</td>
<td>Velocity, Attenuation, Backscattering, Absorption, Hysteresis/harmonics</td>
<td>Elastic constant, stress, micro-structure, Precipitates, voids, micro-cracks, Precipitates, voids, micro-cracks, Dislocations, Plastic deformation, dislocation</td>
</tr>
<tr>
<td>Electro-magnetic</td>
<td>Metals</td>
<td>Permeability, Conductivity, Hysteresis, Upper harmonics, Barkhausen noise, Thermoelectric power, Local magnetic force</td>
<td>Stress, dislocation, plastic deformation, precipitates, voids, Precipitates, voids, micro-cracks, Micro-structure, Micro-structure, Micro-structure, Stress, dislocation, plastic deformation, precipitates, voids, Phase of structure, Micro-structure</td>
</tr>
<tr>
<td>Radiation</td>
<td>Metals, Ceramics</td>
<td>X-ray diffraction, Neutron diffraction, $\gamma$-ray (Mössbauer effect), Positron annihilation</td>
<td>Stress, micro-structure, Micro-structure, Micro-structure, Voids, Plastic deformation, microstructure</td>
</tr>
<tr>
<td>Acoustic emission</td>
<td>Metals, Ceramics, Plastics, Composites, etc.</td>
<td>Events, Countermas voltage</td>
<td>Micro-cracking, embrittlement, Phase deformation, micro-cracking</td>
</tr>
<tr>
<td>Thermography</td>
<td>Composites, concrete, ceramics, etc.</td>
<td>Thermodiffusion</td>
<td>Delamination, voids, micro-crack</td>
</tr>
<tr>
<td>Echo chip</td>
<td>Metals</td>
<td>Hardness</td>
<td>Softening, plastic deformation, embrittlement</td>
</tr>
<tr>
<td>Replica</td>
<td>Metals</td>
<td>Optical observation</td>
<td>Micro-structure</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>Metals</td>
<td>Surface potential</td>
<td>Corrosion, pitting, stress corrosion cracking</td>
</tr>
</tbody>
</table>
2. Research trends

Research into methods to evaluate material degradation can roughly be classified into two kinds: firstly, the development of new methods mainly based on new principles; and secondly, work to improve existing assessment techniques by making them more sensitive and accurate. Here we will introduce examples of the former: non-linear ultrasonic techniques and the terahertz wave. Many scientists have focussed on these two techniques in recent years, and both utilize the non-linear responses of ultrasonic waves.

In the conventional pulse reflection method that uses linear ultrasonic waves, it is very difficult to detect and estimate the size of tiny, closed cracks that have occurred as a result of residual stress or other factors. In the last couple of years a great deal of research has been made into the development of methods that use non-linear ultrasonic wave responses on closed cracks and incomplete junctions and bonded surfaces. Fig. 9.6.1 shows a diagram of an example of how the method works. It is known that the incident ultrasonic wave causes the open and closed parts of the crack surface to vibrate, producing a sub-harmonic wave that has half the frequency of the incident wave as well as a higher harmonic wave of several times the frequency. This phenomenon can be used to evaluate the level of damage in an object. Ohtani et al. have produced images of a secondary higher harmonic wave of creep damage detected in the heat affected zone (HAZ) of a weld on a steam superheater pipe that had been in service for 200,000 hours at a thermal power station, and demonstrated the usefulness of the technique. These kinds of higher harmonic waves are also known to be caused by dislocation movement within materials, and this can be used to determine how far fatigue damage has progressed. Fig. 9.6.2 shows the change in the intensity ratio of the excitation frequency and second/third harmonic waves with respect to the number of cycle ratio in the ultrasonic fatigue test of high-strength steel. The same chart also shows the AE cumulative event count. From the AE signal, the start of macroscopic cracking can be estimated as occurring above $1.18 \times 10^6$ cycles. Before that, the second higher harmonic wave component rapidly increases, and the third harmonic wave decreases. This is thought to be in response to a decrease accompanying the separation and union of pinned dislocations. This is an example of the evaluation of the progress of fatigue deterioration before cracks develop, and illustrates the usefulness of non-linear ultrasonic techniques.

Terahertz waves are electromagnetic waves that have a frequency of 0.1 to 100 THz. Until recently, terahertz waves have been difficult to apply, due to the lack of a suitable signal source, but with advances in technology their use has now become possible. Various effects exist in the terahertz band, including optical phonon scattering in solids, dielectric properties such as ion polarization and orientation polarization, superconductive energy gaps, and various kinds of vibrations of molecules and solids or reciprocal effects between molecules. It is hoped that the use of terahertz waves will allow researchers to learn about what happens inside materials in a way never before possible. Since terahertz waves can pass through ceramics and plastics, and will not harm the human body like X-ray does, they show promise for use in transmission imaging. Reported examples of applications of terahertz waves in non-destructive evaluation include imaging of the inside of the human body and the screening of postal items for drugs, analysis of semiconductor integrated circuits for faults, and checking of the heat-proof tiles on the space shuttle. It is hoped that the characteristics of terahertz waves will make them particularly useful when testing polymers, FRPs, living tissue and ceramic form.

In the creation of a sustainable society that is safe and secure and in harmony with the natural environment, non-destructive evaluation techniques that will allow us to ensure reliability by detecting damage and assessing residual service lifetime, as well as the efficient allocation of costs and resources, will become more important than ever in near future.

References

Materials Outlook for Energy and Environment

New Material Science of the 21st Century toward the Solution of Energy and Environment Issues

~For You Looking to Become a Material Scientist~

Date of publication: 1st edition, 1st impression, 4 July 2008
Publisher: National Institute for Materials Science (NIMS)
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