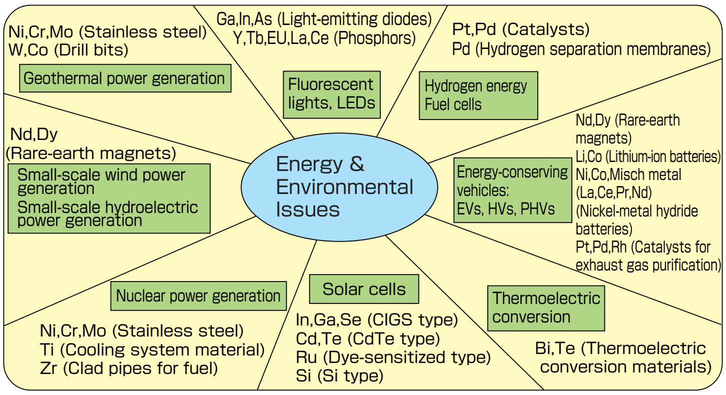
Rare Metals 2

Trends in Rare Metal Issues and Efforts of the Rare Metal Task Force

Rare metal issues

While there is widespread concern over the crisis of the limited availability of energy resources, we must also recognize the seriousness of the problems facing the supply of rare metals due to the fact that most of rare metal deposits are located in extremely limited countries and that development of their substitution is more difficult than in the case of energy, which has several alternatives. Although Japanese manufacturers heavily depend on rare metals, domestic production (especially onshore production) is extremely limited. Below are some of the reasons why issues related to rare metals have become critical.



Energy & Environmental Issues and Rare Metals

・**Demand**

① The rapid economic development of countries with massive populations, such as China and India, is increasing demand for rare metals.

② The IT revolution, globalization of mass production systems (modularization and low labor costs), and huge amounts of capital that can be freely moved around the world have made a rapid increase in global productivity (i.e., a rapid increase in consumption of natural resources) possible.

③ Demand has increased for new products that require rare metals, such as EV and HV, because of policies to deal with energy and environmental issues (“green rare metals”).

・**Supply**

④ An oligopoly for some of the rare metal resources has been created by China and some major mining companies.

⑤ The development of new mineral deposits faces longer lead times and higher costs due to resource nationalism and environmental protectionism.

⑥ Mining of low-grade deposits, which become necessary as high-grade deposits are depleted, require substantial amounts of energy. With existing technologies and rising energy cost, the usability of low-grade deposits is limited.

・**Speculation**

⑦ Enormous speculative funds are searching for alternative investments that can replace investments in stocks and land. Investment in natural resources is a strong candidate.

Because of the above factors, demand for rare metals will rise continuously with a high probability of a surge in the short term, while a rapid increase in their supply is likely to become more and more difficult.

Status during and after the financial crisis

The prices of many rare metals have declined with the fall in demand due to the recession, which began with the financial crisis in the autumn of 2008. However, the above-mentioned factors have not changed at all. In fact, the prices of some rare metals for which there is a strong oligopoly have not decreased. Tight supply and demand of rare metals can be expected with economic recovery, or with the mere anticipation of a recovery. If the supply of even one type of rare metal becomes limited, the manufacturing of products that use it will be constrained. This could cause major damage to an industry as a whole, particularly if the industry is highly competitive internationally.

Efforts of the Rare Metal Task Force

The objective of the AIST Rare Metal Task Force is to support Japan's economic security by developing urgently needed technologies that will have a major impact on the entire flow of rare metals , such as resource exploration, technologies to reduce rare-metal consumption, technologies to develop the substitutes for rare metals, and recycling technologies, utilizing AIST's research potential and accumulated technological know-how.

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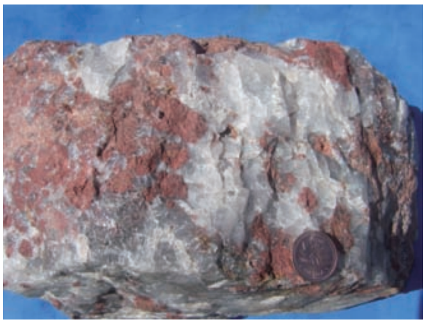
Exploration of Rare Metal Resources

Background of rare metal exploration

There are two types of metal resources. One type is consumed in massive quantities as vital industrial materials. These include iron, copper, and aluminum, to name only a few. The other type, referred to as rare metals, sees very little consumption in quantitative terms but is essential for high-technology industries. In particular, rare-earth elements (REE) are critical metals for magnets in electric motors used for hybrid vehicles and consumer electronics. As such, their consumption has been increasing every year, and a stable supply of the REE is vital to Japan's industrial development. Unfortunately, however, the stability of their future supply is in question, because more than 90 % of REE are produced in China and the supply is easily impacted by the political, economic, and mining industry conditions there. With the above as the backdrop, the Mineral Resource Research Group of the Institute for Geo-Resources and Environment (GREEN) is conducting resource explorations overseas to diversify the supply chain of REE outside of China. Details of the REE exploration activities of the research group are discussed in the May 2008 issue[1], as well as on the pages 4 and 5 of this issue. Here, I will discuss the concepts behind this undertaking.

Field investigation at Canada's Thor Lake deposit
Long shadows are seen even at midday because the site is located in the Arctic.



Mineral ore at Thor Lake
Abundant rare-earth elements are contained in the reddish-brown mineral (bastonesite).

What is resource potential evaluation?

The aim of the resource exploration activities of the Mineral Resource Research Group is to evaluate the resource potentials of yet-to-be-developed mineral deposits. The term *resource potential* refers to the prospects for developing a mineral deposit based on the grade and total reserve of the ore of the targeted element. A resource potential needs to receive an evaluation of high quality in order to minimize the risks associated with mine exploitation and make stable production possible. Generally, the quantity of ore reserves in a deposit is calculated based on information obtained from the three-dimensional structure of the deposit and the ore distribution in terms of its grade, which can be gathered from surface exploration, drilling surveys, and chemical analyses. In the case of a REE deposit, however, it is of critical importance to understand the form of existence of the REE concerned in addition to the above aspects. For example, if REE is contained within carbonate minerals, it can be easily extracted with acid treatment, but if it is contained in refractory minerals such as zircon, extraction will be difficult to justify in a conventional business case study. Therefore, those parts that are difficult to extract must be excluded from the calculated quantity of the ore reserve. An accurate resource potential evaluation of a rare earth deposit should thus include mineralogical information on how many parts per million of REE are contained within what mineral.

Future developments

The overseas resource exploration activities of the Mineral Resource Research Group are being conducted in collaboration with private enterprises and the Japan Oil, Gas and Metals National Corporation (an independent administrative institution). We are in the process of targeting several promising REE deposits, and are moving forward with the survey work in the hope of starting a new mine by 2014.

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Types and Characteristics of Rare Earth Deposits

Current status of REE resources

Rare earth elements (REE) are considered to be seventeen elements consisting of lanthanoids (lanthanum to lutetium), yttrium, and scandium[1]. Demand for REE has been increasing in recent years for use as catalysts in automotive applications and as rare earth magnets. It is predicted that the demand will continue to rise as hybrid vehicles become more prevalent. However, more than 96 % of REE resources are imported from China[2]. In particular, heavy rare earth elements (HREE) have lower crustal abundance compared with light rare earth elements (LREE). In addition, the types of deposits that supply HREE are limited. Therefore, a discovery of new mineral deposits is essential for stabilizing the supply of REE resources (especially HREE resources)[3]. We are currently investigating resource potential in various REE deposits .

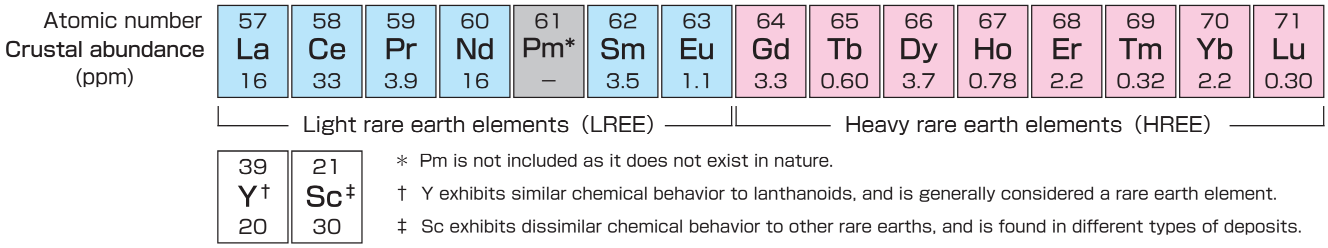
Types of deposits supplying REE resources

Deposits that supply rare earth resources[4] can be divided into two categories; igneous deposits formed by igneous rocks or associated hydrothermal activity and weathering deposits created from weathered rocks (Fig. 2). Examples of igneous deposits include carbonatite deposits, alkali rock-related deposits, and hydrothermal iron deposits. Carbonatite which is an igneous rock consisting mainly of carbonate mineral is an important source of REE resources. China's Maoniuping deposit and the Mountain Pass deposit in the U.S.A. are two of the major carbonatite deposits. Alkali rocks often occur with carbonatites, and can form HREE-rich deposits. Canada's Thor Lake deposit is representative of the alkali rock-related deposits. A hydrothermal iron ore deposit has many characteristics. China's Bayan Obo deposit, which is the largest deposits in the world, is a well-known hydrothermal iron deposit.

Examples of weathering deposits include laterite deposits, ion-adsorption type deposits, and placer deposits. Laterite here refers to red soil that becomes rich in REE due to decomposition of carbonate minerals by weathering. Enrichment of REE by the weathering process is a marked characteristic of this type. Australia's Mount Weld deposit is a representative example. Ion-adsorption type deposits exist only in southern China. Most of HREE supply comes from this region. This type of deposit is characterized by REE adsorption onto the surface of clays and other materials in weathered granite soil. The Longnan deposit and Xunwu deposit are representative examples of such deposits. Placer deposits are formed by sedimentation of concentrated heavy minerals through weathering and erosion of rocks in locations such as seashores. They are rich in ilmenite, but also often contain monazite, which is one of REE minerals. The Kerala region in southern India and Richards Bay in South Africa are examples of areas of placer deposits.

Minerals containing REE

The ore minerals containing REEs consist of carbonates, phosphates, oxides, and ion-adsorption clays. Bastnaesite [REE(CO_3)F] is a representative REE mineral among carbonate minerals and is contained in carbonatite deposits. Monazite [(REE,Th)PO_4] is representative of phosphate minerals. It is commonly found in placer deposits and igneous deposits. The oxides include loparite [$(REE,Na,Ca)_2(Ti,Nb)_2O_6$], which is contained in alkali rocks. With ion-adsorption clays containing kaolinite [$Al_2Si_2O_5(OH)_4$] and other materials, as REE are electrically adsorbed onto the mineral surfaces, they can be recovered by ion exchange using a mild acid without decomposing the minerals themselves. Although there are several silicate minerals containing REE, they are rarely used as resources because of the high cost of extraction due to their generally tough crystal structure.



Atomic number	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	La	Ce	Pr	Nd	Pm*	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Crustal abundance (ppm)	16	33	3.9	16	–	3.5	1.1	3.3	0.60	3.7	0.78	2.2	0.32	2.2	0.30
	Light rare earth elements (LREE)							Heavy rare earth elements (HREE)							

39	21
Y†	Sc‡
20	30

* Pm is not included as it does not exist in nature.

† Y exhibits similar chemical behavior to lanthanoids, and is generally considered a rare earth element.

‡ Sc exhibits dissimilar chemical behavior to other rare earths, and is found in different types of deposits.

Fig. 1 Types of rare earth elements (REE) and crustal abundance

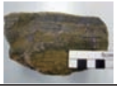
	Types of deposit	Representative examples of deposits (country)		Dominant REE resources
Igneous deposits	Carbonatite deposits	Maoniuping (China) Mountain Pass (U.S.A.) – currently not operating		LREE
	Alkali-rock-related deposits	Lovozero (Russia) Thor Lake (Canada) – not yet developed		LREE HREE
	Hydrothermal iron ore deposits	Bayan Obo (China)		LREE
Weathering deposits	Carbonatite-derived laterite deposits	Mount Weld (Australia) – not yet developed		LREE
	Ion-adsorption type deposits	Longnan and Xunwu (China)		LREE HREE
	Placer deposits	Kerala (India) Richards Bay (South Africa) – not yet developed		LREE

Fig. 2 Types of REE-supplying deposits and their characteristics
The photos show REE ores and deposits.

Fig. 3 Outcrop of weathered crust of granite in Laos
Ion-adsorption type REE mineralization is partly identified.

Challenges surrounding REE resources

We need to continue studying REE deposits, because systematic studies of such deposits are relatively uncommon in the world compared with those targeted at base-metal and precious-metal ore deposits. Identification of HREE deposits and of REE minerals are two of the challenges facing research on REE deposits. The first challenge is to identify and discover deposits capable of supplying HREE, which are relatively rare compared with LREE. For example, ion-adsorption type deposits, which supply HREE, were previously only found in China, but such mineralization has begun to be locally discovered in other countries[5] (Fig. 3). We also need to study deposits that may be enriched in HREE, such as alkali rocks and placer deposits. The second challenge is to clarify the existence form of REE minerals, and quantitatively evaluate them. Although REE are contained within a variety of minerals, the majority of silicate minerals are difficult to utilize as resources. We also know that minerals containing REE occur between the grains and cracks of other minerals[6]. Therefore, we need to evaluate whether REE exist within minerals that are suitable for mineral processing and refining, and whether they can be extracted economically. Resolution of the above issues will lead to the development of more REE deposits.

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Reduction of Platinum Usage by a Core-Shell Structure

Necessity of reducing the use of platinum in fuel cells

Fuel cells, which have been attracting attention as a clean energy source in recent years, can be classified into several different types depending on the electrolyte used. Among the types of the fuel cells, the polymer electrolyte fuel cell (PEFC), which uses a proton-conducting polymer membrane as the electrolyte, can operate at a low temperature below 100 °C. Thus, power sources for portable electronic products and automobiles are among the targeted uses of PEFC.

There are however, issues associated with this type of fuel cell, specifically because it operates at a low temperature. Generally, the rate at which a chemical reaction takes place rapidly decreases with lowering temperature. A highly active catalyst is therefore required in order to ensure a sufficient reaction rate. In a PEFC, an oxidation reaction of hydrogen occurs on the anode and a reduction reaction of oxygen takes place on the cathode. With the existing technology, platinum must be used as the catalyst for both electrodes.

Platinum is a very scarce element, as is well known. Worldwide annual production of platinum is approximately 230 tons, and reserves of platinum-group elements are estimated to be 63,000 tons.[1] At the current pace, these reserves would last for close to 200 years. However, it is said that once PEFCs become the mainstream, platinum use will increase to 10 times the current level or more depleting the reserves in less than 20 years. The issue of the supply of platinum-group elements is extremely serious, especially considering the fact that approximately 80% of these elements is exclusively distributed in the Republic of South Africa[1] .

Core-shell catalyst technology

With the above as the backdrop, there are various efforts worldwide to significantly reduce the use of platinum in PEFCs. The Catalytic Nanomaterials Group of the Materials Research Institute for Sustainable Development is examining the effectiveness of "core-shell technology", which is one of the methods for reducing the use of platinum as an electrode catalyst. The application of core-shell technology to a catalyst involves replacing the interiors of the metal particles (core), which do not directly contribute to the catalytic reaction, with a different material, while leaving the surfaces of the particles (shell) consisting of a highly active material (platinum).

Increasing the specific surface area of metal particles generally improves the efficiency of a supported metal catalyst. Hence, it is a common practice to reduce the diameter of the metal particles. However, reducing the diameter does not yield the desired effect with a PEFC. The key is the support material that holds the metal particles. Ultrafine carbon particles forming a substance called carbon black

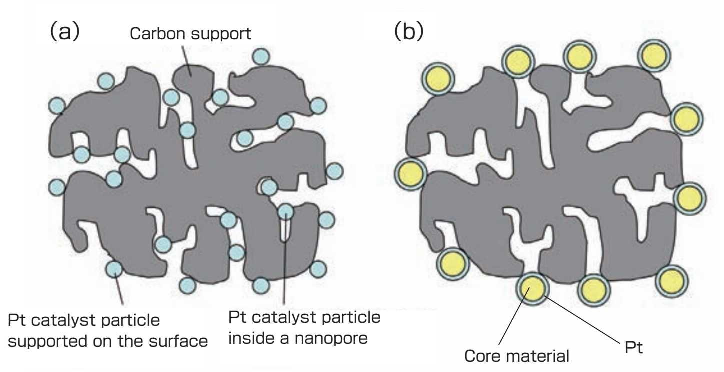

Fig. 1 Platinum catalyst particles supported on carbon black
(a) If the particle diameter is too small, the particles become trapped in the nanopores and do not contribute to the reaction.
(b) The platinum utilization can be effectively improved by the core-shell technique without reducing the particle diameter.

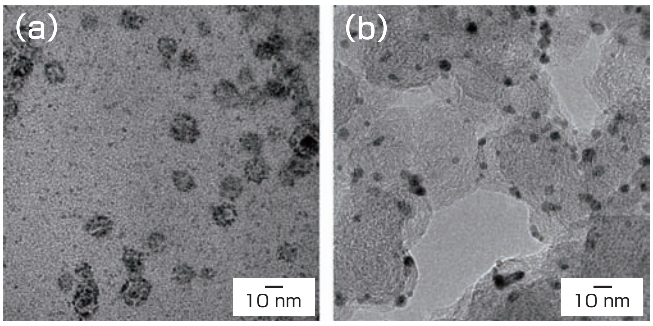

Fig. 2 (a) TEM image of catalyst nanoparticles with silver core and platinum shell
(b) TEM image of catalyst nanoparticles with gold core and platinum shell supported on carbon black

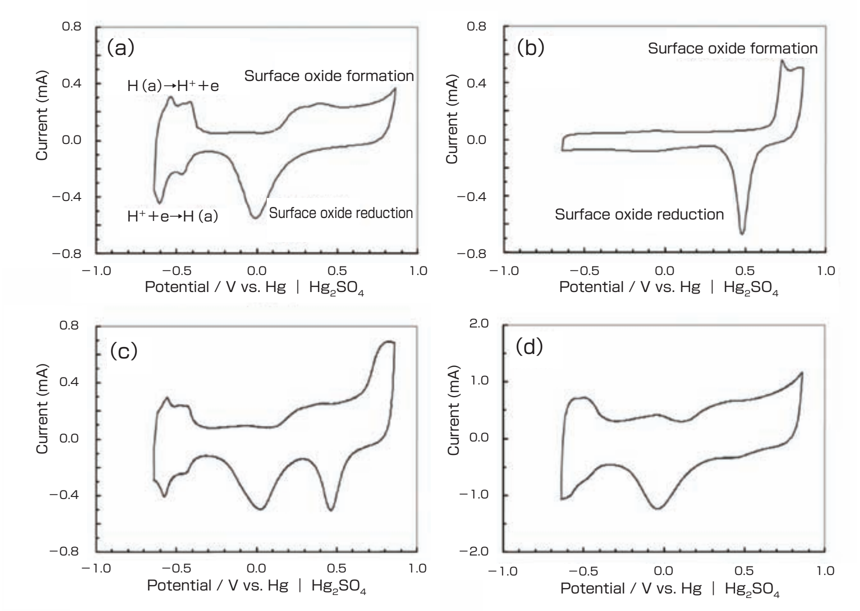

Fig. 3 Cyclic voltammograms of
(a) platinum nanoparticles
(b) gold nanoparticles
(c) mixture of platinum and gold nanoparticles
(d) gold core-platinum shell nanoparticles

are used as the catalyst support in a PEFC due to their conductivity. These carbon particles have a lot of nanopores, and if the metal particles are too small, they become trapped in these pores. The trapped particles are unable to contribute to the reaction (refer to Fig. 1(a)). Core-shell technology is one of the methods to improve the platinum utilization without reducing the particle size, avoiding the above phenomenon (Fig. 1 (b)). The core material used would be cheaper and with less risk of supply disruption than platinum.

Production and evaluation of core-shell catalysts

Figure 2 (a) shows a transmission electron microscope (TEM) image of nanoparticles, produced by a method called liquid-phase reduction, that are each made up of a silver core and a platinum shell. Several particles with a diameter of approximately 10 nm can be observed. The lighter colored interior is silver, and the darker colored surface is platinum. Figure 2 (b) shows a TEM image of nanoparticles on a carbon black support, consisting of gold cores and platinum shells. The diameter of the majority of the particles is from 2 to 4 nm, similar to that of commercially available platinum catalysts. It is difficult to directly verify the core-shell structure using a TEM image, because the atomic numbers of gold and platinum are close to each other. However, we can verify the structure electrochemically, as follows. Figures 3 (a), (b), (c), and (d) show the results of cyclic voltammetry of platinum nanoparticles, gold nanoparticles, a mixture of platinum and gold nanoparticles, and gold core-platinum shell nanoparticles, respectively, all on a carbon black support. The plots (cyclic voltammograms) obtained in this method show a unique wave shape for each sample, based on the electrochemical characteristics of the surface materials. Apparently, (d) shows an almost identical wave shape to (a), even though the core-shell particles contain similar amount of platinum and gold. It can therefore be concluded that the nanoparticles are in the core-shell structure with platinum covering most of the outer surface.

Factors that will determine the performance of core-shell catalysts include the nanoparticle diameter, core material, core-to-shell ratio, metal loading, and production method, to name only a few. Our group will systematically alter these variables and evaluate the performance. In particular, we will focus on the reduction of platinum use, and explore the limits and possibilities of core-shell technology.

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Development of Iron-based Thermoelectric Material as an Alternative to Bismuth Telluride Alloy

Massive amounts of waste heat

In Japan, several hundred million kL (crude oil equivalent) worth of primary energy is consumed annually. However, in the process of converting primary energy into secondary energy such as electricity, more than 60 % of the primary energy is released into the atmosphere as waste heat. Effective use of this massive amount of waste heat is being sought against the recent social background, such as concerns over the future supply of energy and the emergence of environmental issues.

However, it is difficult to effectively utilize waste heat by means of conventional energy conversion techniques—driving a turbine to create electricity, for example—because the sources of waste heat, such as power plants, factories, and automobiles, are widely scattered, and moreover the majority of this waste heat is at a low temperature of less than 200 °C. In order to effectively utilize this scattered, small-scale, low-temperature waste heat, "thermoelectric generation," which has a conversion efficiency independent of the energy scale and is capable of generating electricity from thermal energy of any temperature, may provide a solution.

The rare metal issue in thermoelectric power generation

Thermoelectric generation utilizes the temperature difference between thermoelectric materials to generate electricity. Principally, a basic component of thermoelectric generation system is an electrical circuit consisting of connections of p-type and n-type thermoelectric materials in series, as shown in Fig. 1. Such a setup can generate electricity when one end of the thermoelectric materials is heated using waste heat, thus making recovery and reuse of the energy possible. An example of a highly effective thermoelectric material for temperatures of 200 °C or below is an intermetallic compound using bismuth (Bi) and tellurium (Te). Active research has been conducted on Bi-Te thermoelectric material, and devices with a conversion efficiency of several percent have already been developed.

However, both Bi and Te are rare metals. In addition, Te has lower estimated reserves than platinum, and Bi is unevenly distributed. The use of these materials as the basic elements in thermoelectric power generation devices, which would be required in large quantities to utilize waste heat sources that are scattered in various locations, may therefore be problematic. Moreover, the Bi-Te system can only be used in a limited range of environments because of its low chemical durability against oxidation and low mechanical strength. Hence, at AIST we are developing iron-based thermoelectric materials that are less resource-restrictive as replacements for the Bi-Te compound, in order to promote effective utilization of low-temperature waste heat for practical applications.

Research and development of iron-based thermoelectric materials

Fe_2VAl alloys with a Heusler crystal

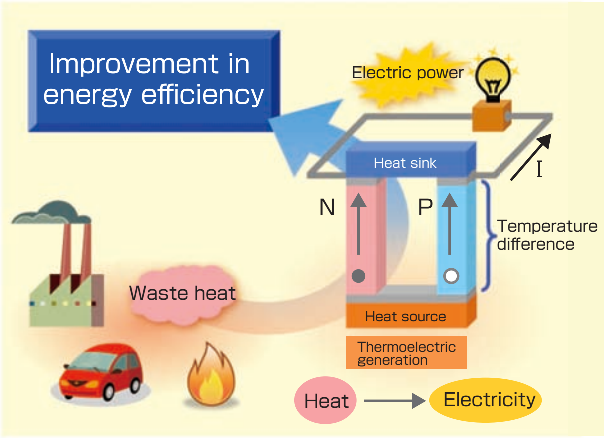


Fig. 1 Concept of waste heat recovery using thermoelectric generation device.

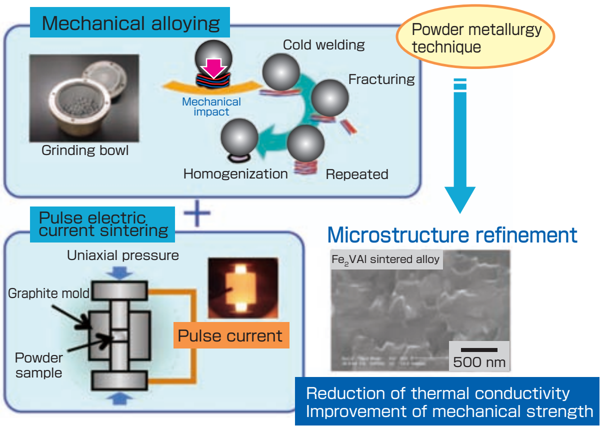
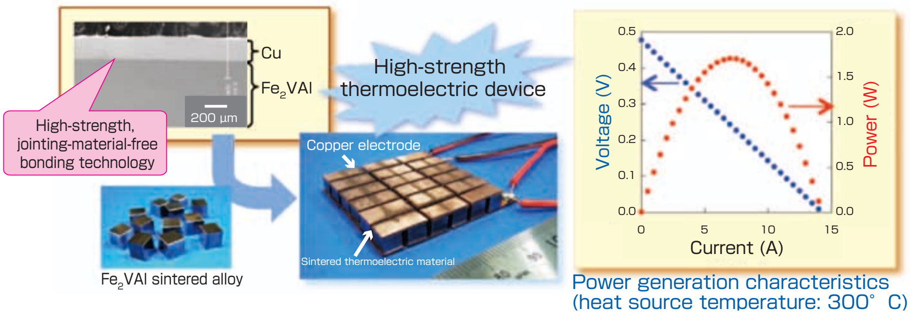


Fig. 2 Powder metallurgy technique and microstructure of Fe_2VAl sintered alloy



Power generation characteristics (heat source temperature: 300° C)

Fig. 3 Thermoelectric device developed with direct electrode joining technique and its power generation characteristics

structure exhibit superior power generation performance comparable to that of conventional thermoelectric materials, such as the Bi-Te system, at room temperature by regulating valence electron concentration via partial substitution of elements. They are stable materials, with a high melting point of 1500 °C along with good oxidation resistance. However, Fe_2VAl alloys are not suitable for practical application as they are because of their relatively high thermal conductivity, resulting in the difficulty to obtain large temperature difference and in a low energy conversion efficiency.

AIST has therefore been attempting to enhance the thermoelectric properties of Fe_2VAl alloys by controlling microstructure through a powder metallurgy technique, as shown in Fig. 2. First, we succeeded in obtaining the alloyed powder, which has the nanometer-sized internal structure, by using a mechanical alloying method. We achieved this by determining the conditions that allow stable repeated mechanical pulverizing and mixing. Next, the mechanically alloyed powder was sintered rapidly using a pulse-current sintering technique to suppress grain growth during heat treatment and to obtain a fine microstructural bulk material. We were then able to obtain sintered alloy made of nanometer-order crystal grains. In the microstructured sintered alloy, we succeeded in lowering the thermal conductivity through a scattering effect at the grain boundaries. The structural refinement also improved the durability of the material by dramatically increasing its mechanical strength.

Development of devices for practical application

Electrode connection is one of the most important factor of research for the development of practical thermoelectric devices. For the construction of conventional thermoelectric devices, jointing materials, such as solder, were used for the connection between electrode and thermoelectric material. However, this technique spoils the high mechanical strength characteristic of Fe_2VAl alloy, because jointing materials usually have a low melting point and low mechanical strength. We succeeded in developing a technique for directly joining Fe_2VAl sintered alloy with copper electrodes that has high mechanical strength (Fig. 3). We have verified that as much as 1.7 W of power can be obtained when the thermoelectric device is used with a heat source of 300 °C. Moreover, the electrical resistance at the connection is negligible, resulting in minimal power loss at the connection.

With its comparably higher mechanical strength, the newly developed thermoelectric device can potentially be used in harsh environments such as the internal combustion engines of cars, which are subjected to vibration and extreme heat cycles. In addition, because of the reduction of reinforcements and other unnecessary parts with this new jointing technique, simplification of the structure along with increased design freedom can be realized when designing for practical applications. The device is economical and suitable for mass production because it is made up of elements that are cheaper and have a more reliable supply compared with conventional thermoelectric materials. We hope that it will contribute to the dissemination of thermoelectric conversion technology. AIST will continue its efforts to enhance the performance of thermoelectric materials and explore applications for waste heat.

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Development of Highly Effective Extractant for Platinum Group Metals

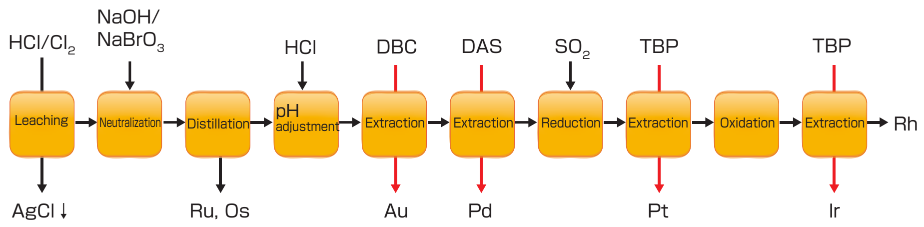
Separation and purification processes using solvent extraction

In recent years, platinum group metals (PGMs) have been increasingly used in industry, e.g., electrical systems and devices, catalysts, etc; therefore, it has become important to recover PGMs from their wastes. The solvent extraction (liquid-liquid extraction) method is mainly employed for separation and purification processes of the PGMs. This method is based on the partition of a solute between two immiscible phases (i.e., aqueous and organic phases). Typically, an organic compound (extractant) with high affinity to a specific metal diluted with an organic solvent (diluent) is used as an organic phase. Hence, the successful outcome of solvent extraction depends entirely on the selection of a suitable extractant. Moreover, for industrial applications, separation properties like extraction rate and durability need to be considered in addition to basic capabilities such as extractability and selectivity.

Currently, much of the metal recycling from PGM-containing wastes utilizes separation and purification processes consisting mainly of solvent extraction that were developed by mining companies. In particular, processes based on that developed by INCO (Fig. 1)[1] [2] are widely used. In the INCO process, silver chloride (AgCl) is precipitated at the leaching stage using chlorine gas (Cl_2) + hydrochloric acid solution (HCl). Next, ruthenium (Ru) and osmium (Os) are separated by distillation, and gold (Au), palladium (Pd), platinum (Pt), and iridium (Ir) are separated by solvent extraction. Lastly, rhodium (Rh) is recovered from the residual solution. The extractants used here are excellent for the selective separation of PGMs, but many of them have issues concerning extraction rate, durability, etc. Another drawback is economic inefficiency due to the long retention period of rhodium, which is the most expensive of the PGMs. We are developing PGM extractants, and have discovered effective organic compounds for extracting palladium or rhodium.

Rapid separation of palladium using an oxidation-resistant extractant

Di-*n*-hexyl sulfide (DHS) is one of the most popular extractants used in industry for the palladium separation. DHS exhibits a good capability for the separation of palladium over platinum, but the palladium extraction is very slow. In addition, the palladium extractability with DHS deteriorates with its long-term use. A new palladium extractant with a high extraction rate and superior durability is therefore desired. We have found that thiodiglycolamide (TDGA) shows excellent extractabilities for palladium[3][4]. TDGA has a sulfide having a high affinity with palladium and two *N*,*N*-disubstituted amides, which is simply synthesized and soluble in various organic solvents. As seen in Fig. 2, the extraction rate of palladium with TDGA is extremely high compared with that with DHS. TDGA can also selectively extract palladium over platinum. Although the extraction percentage (*E*%) of palladium with DHS is severely reduced by contact with a strong acid solution (0.75 mol/L nitric acid + 2.25 mol/L hydrochloric acid), that with TDGA hardly changes. The FT-IR spectra show sulfoxide formation by the oxidation of the sulfide in DHS after contact with the strong acid solution, but not in TDGA, indicating that TDGA is more durable than DHS. Additionally, TDGA exhibits similar properties to DHS in regard to the back-extraction and loading capacity. Thus, TDGA has good properties for practical use along with its prominent basic extractabilities; we are now studying practical applications for this extractant.



DBC: Dibutylcarbitol, DAS: Dialkylsulfide, TBP: Tri-*n*-butyl phosphate

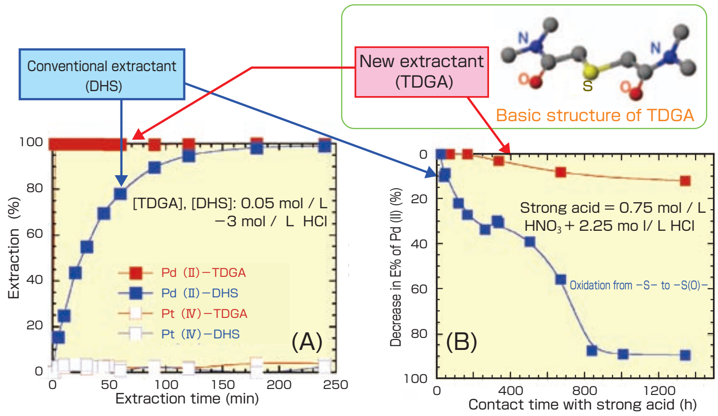
Fig. 1 Metal separation and purification process by INCO
Solvent extraction is mainly used.

Development of a new extractant for rhodium

In the separation and purification

processes of PGM, as mentioned earlier, rhodium is recovered from the residual solution after the other PGMs are separated. This is because there has been no effective rhodium extractant developed for industrial use. Rhodium exists as anion complexes in relatively highly concentrated hydrochloric acid solutions, which are nearly impossible to extract. Generally, the application of an ion-pair extraction would be considered for extracting anion complexes, but additional effects to the ion-pair reaction seem to be required for rhodium extraction.

We synthesized a tertiary amine containing two *N*,*N*-disubstituted amides: *N*-*n*-hexyl-bis(*N*-methyl-*N*-*n*-octylethylamide)amine (HBMOEAA). We then studied the extraction behavior of the PGMs (rhodium, palladium and platinum) from hydrochloric acid solutions. As shown in Fig. 3, HBMOEAA extracts 80% of rhodium at 1 to 2 mol/L hydrochloric acid. This *E*% value is the highest ever obtained in rhodium extraction from relatively highly concentrated hydrochloric acid. As for the palladium and platinum extraction, high *E*%s from 0.5 to 10 mol/L hydrochloric acid are obtained, whereas rhodium is hardly extracted at about10 mol/L hydrochloric acid. This means that palladium, platinum and rhodium are simultaneously extracted at 1 to 2 mol/L hydrochloric acid, and then rhodium alone is back-extracted into the aqueous phase by bringing the organic phase into contact with a 10 mol/L hydrochloric acid solution. This result of recovering rhodium before palladium and platinum is groundbreaking. The next research will focus on the extraction mechanisms and the characteristics required for practical application.



TDGA = *N*,*N*'-dimethyl-*N*,*N*'-di-*n*-octyl-thiodiglycolamide

Fig. 2 Comparison of palladium extraction using conventional extractant DHS with that using new extractant TDGA (A: extraction time, B: stability against strong acid)

Compared with DHS, TDGA can selectively extract palladium more rapidly and the extractability for palladium is less affected by the strong acid.

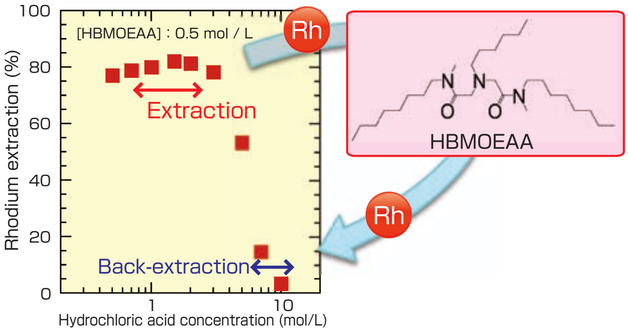


Fig. 3 Rhodium extraction from hydrochloric acid solution with HBMOEAA

Extraction/back-extraction can be carried out by adjusting the concentration of hydrochloric acid.

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