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PRESENT STATUS OF RESEARCH AND DEVELOPMENT ON THERMOELECTRIC POWER GENERATION TECHNOLOGY IN JAPAN

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- *Thermoelectric technology, in particular, thermoelectric power generation technology, has been expected to play an important role in the environmental conservation, energy security and stimulus to industry in the future in Japan. The paper summarizes an overview of the present status of research and development on thermoelectric power generation systems and the related thermoelectric materials in Japan. The progressing development activities have been carried out by the project members of private companies after finishing 5-year national project for Advanced Thermoelectric Conversion Systems. The demonstration system experiments using practical heat sources such as a 500kW diesel engine cogeneration system and a 10 t/day sewage treatment plant have been achieved. In parallel with these experiments the small scale demonstration system experiments have been also carried out using the hot springs and the waste heat from motorcycle. The research on various kinds of thermoelectric materials has been energetically carried out by universities and national research institutes mainly. Several topics of scientific results on advanced materials such as layered oxides, low-dimensional nanostructured oxide, half-Heusler compound and so on from the view point of environmentally friendly materials and nanosturucture approach are briefly introduced. The investigation including innovative thermoelectric material research and waste heat recovery systems has been achieved as one of the forthcoming national projects by AIST (National Institute of Advanced Industrial Science and Technology).*

Introduction

Thermoelectric technology has been expected to play an important role in the three fields: those are 1) the environmental conservation such as reduction of carbon emissions, 2) contribution to energy security due to energy conservation and conversion of solid waste to domestic energy resource, and 3) stimulus to industry as new thermoelectric industry in the future in Japan. The 5-year national project for Advanced Thermoelectric Conversion Systems had been carried out in the New Global Warming Prevention Technology Program, aiming the establishment of the high-performance thermoelectric power generation system technology for the waste heat recovery from the industrial and the private sectors [1]. It was financially supported by the New Energy and Industrial Technology Development Organization (NEDO) and Ministry of Economy, Trade and Industries (METI) from April 2002 to March 2007. In 2007 the Department of Project Evaluation in NEDO evaluated our project as an ex post facto assessment to be successful with the satisfactory achievement of the targets in the project. Then, for two years after the project, the member companies of the project have been carrying out the preparation for the commercialization phase.

The research on various kinds of thermoelectric materials has been intensively achieved aiming an enhancement of the thermoelectric performance by universities and national research institutes mainly supported by Ministry of Education, Culture, Sports, Science and Technology and NEDO. Especially, layered oxides such as $NaCo_2O_4$, $Ca_3Co_4O_9$ and so on as a novel thermoelectric material have been found during the past several years in Japan. The dimensionless figure of merit was reported to be more than 1.0 for a single crystal of *Ca-Co-O*(*p*) and *Bi-Sr-Co-O*(*p*) and 0.7-0.8 for ceramic $NaCoO_2$ (*p*) at 700 K. Recently novel processing strategy such as nanoblock integration to layered oxides has been proposed by Prof. K. Koumoto's group in the CREST project supported by Japan Science & Technology Foundation при 800–1000 K [2].

An overview of the present status of research and development on thermoelectric power generation systems and on the related thermoelectric materials in Japan is introduced in the paper.

Demonstration experiments for thermoelectric power generation systems

In the above-mentioned national project three types of the cascade thermoelectric modules up to 850 K in high electrode temperature and two types of high performance *Bi-Te* class thermoelectric modules at 523 K in maximum electrode temperature had been developed including durability tests. Moreover, four types of advanced thermoelectric power generation systems had been developed for waste heat recovery from an industrial electric heating furnace using a radiation heat transmission, from a simulated diesel engine cogeneration system using thermo-siphon type heat exchanger system, from a small model of a large scale electric transformer facility, and from a projector lamp reflector. Some of these experimental facilities were small scale models and others were tested using simulated heat sources.

In the next phase to the realization of the thermoelectric power generation system for practical use it is necessary to confirm the technological viability by the demonstration tests applied to practical rejected heat sources.

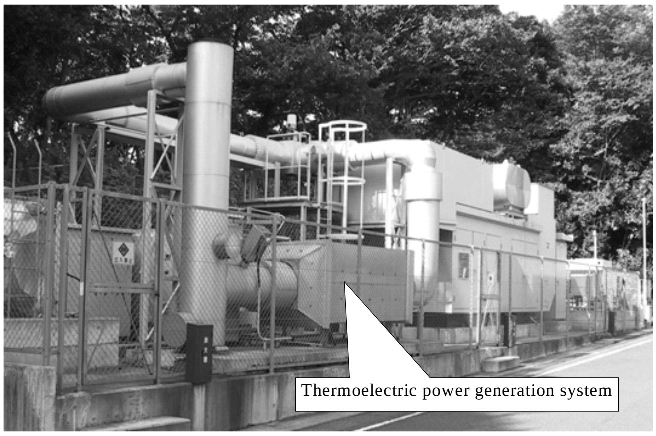

Fig. 1. 1kW class demonstration test facility installed in a 500 kW diesel engine cogeneration system.

KOMATSU Ltd. has carried out the demonstration test on a 1kW class thermoelectric power generation system using real exhaust gas for a 500 kW diesel engine cogeneration system as shown in Fig. 1. Eight fin-plate type heat exchanging units mounted on 8 thermoelectric modules (44.5 mm × 44.5 mm, element size; 1.95 mm × 1.95 mm × 2.15 mm) of the advanced *Bi-Te* thermoelectric elements (161 couples in a module) to extract the heat from exhaust gas. Consequently 64 modules (=8 units, 4 stages) are installed. The fin pitch for each stage is arranged to be 13 mm, 7 mm, 4 mm, and 3 mm in order from inlet to outlet to extract the amount of heat from the gas at the same level. The heat transfer coefficient is about 1 kW/m^2K at the hot side. The inlet gas temperature is typically 673 K and outlet temperature is about 473 K. The amount of gas flow rate is used from 20% to 40% of overall exhaust gas flow rate (42.4 m^3/min.) for a 500 kW diesel engine. Gas flow velocity is 5–15m/s. 8 units of the water cooled plate type heat exchangers are installed to reject the heat from thermoelectric modules. The water flow rate is about 100 l/min. each, and the heat transfer coefficient for pin-fin type heat exchanger is 12 kW/m^2K. The power output characteristics at the first stage unit are shown in Fig. 2. The maximum power output is 146 W (Optimum load current is 2.75 A and Open circuit voltage is 102 V.) at 683 K of gas temperature and 9.2 m/s of gas flow velocity. At the 16.7 m^3/min. of total gas flow rate, overall power output is obtained 1060 W. Figure 3 shows the variation of heat input for thermoelectric modules on run- time. The heat input is gradually decreased with run-time due to the soot deposition and reached to be a saturated level after around 100 h. The degradation of the power output is 30%, so that it suggests that soot blower, for example, will be needed for practical use.

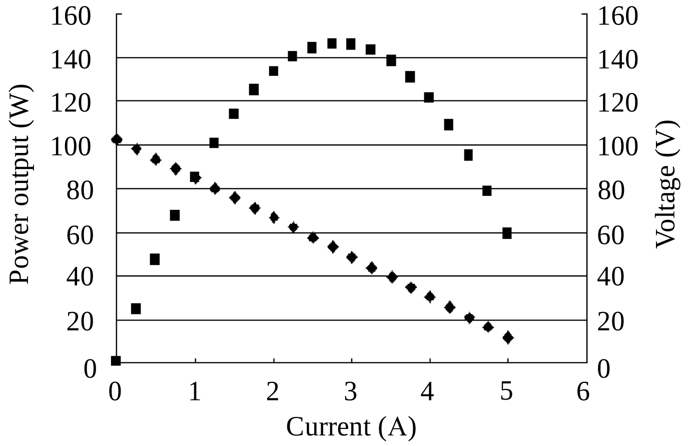

Fig. 2. Characteristics of thermoelectric power output for one unit at the first stage.

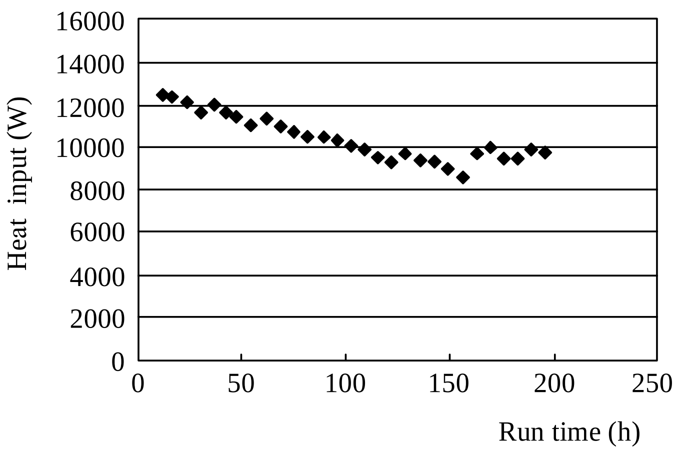

Fig. 3. Variation of heat input on run time.

UBE INDUSTRIES, Ltd. had achieved the demonstration test installed in the incinerator system of sewage treatment plant of 10 tons per day in capacity as shown in Fig. 4. Thermoelectric power generation system is installed at the bypass line between outlet of air pre-heater and inlet of gas pre-heater to prevent exhaust gas to turn to white smoke. The gas temperature at the inlet of the test section is estimated 808 K and flow rate is 10–12.5m^3/min. The test section consists of three series connection of the power generation unit as shown in Fig. 5, where 4 thermoelectric modules are put between 4 sheets of water cooling plate and gas heat exchanger block. Consequently 12 pieces of thermoelectric modules based on *Bi-Te* class elements are installed in the system. The module size is 152 mm×298 mm. As the peculiar point of Ube's module the size is big to reduce the cost of the installing and production processes. The running mode depends on the incinerator operation as shown in Fig. 6, which is start-up and shut-down for every week. During the 18-month run the power output was found to be very stable as shown in Fig. 7. The figure shows the relationship between power output and open circuit voltage. All data are plotted in the figure, and it can be seen that all data are put on a nearly single line. It means that the degradation of module performance has been negligible, because of no deterioration of thermoelectric modules.

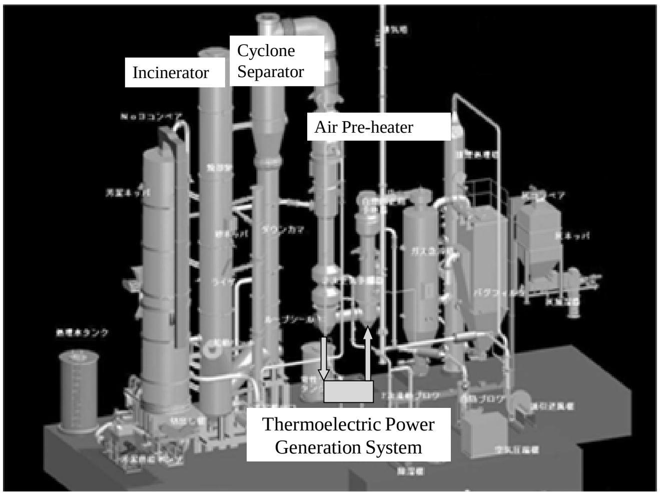

Fig. 4. Demonstration test facility installed real incinerator system of sewage treatment plant.

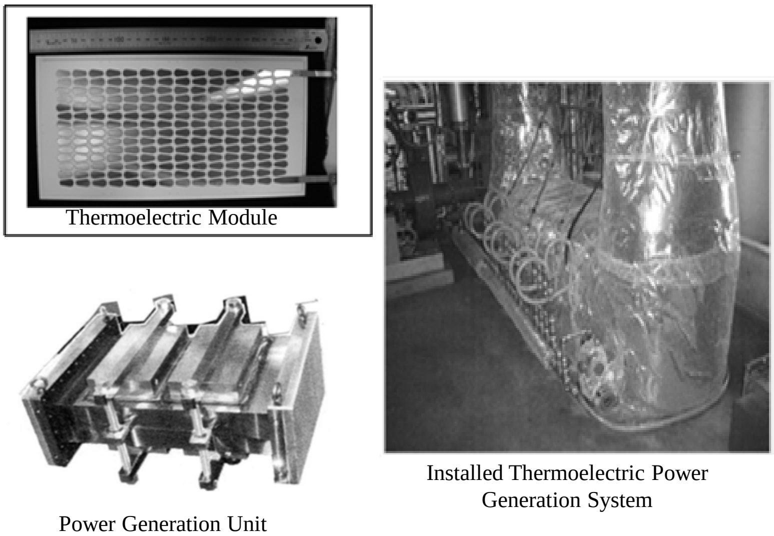

Fig. 5. Thermoelectric module, unit and installed power generation system.

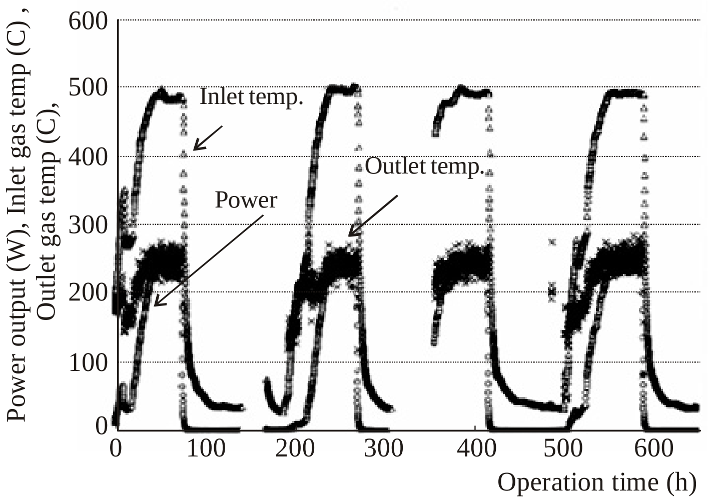

Fig. 6. Characteristics of demonstration system on operation time.

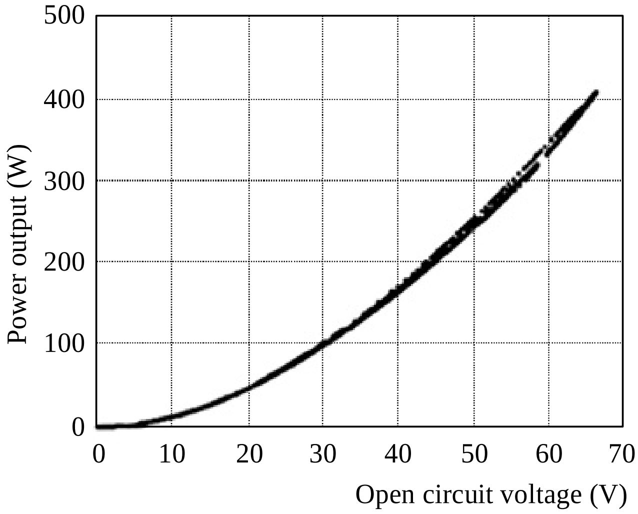

Fig. 7. Accumulated relationship between power output and open circuit voltage during overall operation.

Toshiba Corporation has achieved a 150 W class demonstration test using real hot springs at Kusatsu, Gunma Prefecture located about 170 km in the north far from Tokyo. The temperature of the hot springs, of which *pH* is 2, strong in acidity, is 368 K. Hence, four sets of the heat exchanging plates are made of Ti. The river water is used as a coolant. 5 sets of water cooling plates are installed, of which are made of stainless steel. The thermoelectrics layers consists of 2 parallel-connection units which consist of 20 series-connection thermoelectric modules. Each thermoelectric layer is inserted between hot heat exchanging plate and water cooling plate as shown in Fig. 8. The power output has been continuously generated 150 W using 8 thermoelectric layers, that is, 320 pieces of *Bi-Te* thermoelectric modules. The non-stop run test has been continued to be operated more than 20,000 h. The generated power has been consumed for TV, LED illumination lamps, indicator panel and so on for public relations. Figure 9 shows the relationship between the electricity output per unit area and operating time for thermoelectric power generation based on the hot spring in Kusatsu as compared with a commercial 4 kW photovoltaic power generation unit for residence. It shows that a thermoelectric power generation is obviously superior to a photovoltaic system. Toshiba Corporation has also proposed the conceptual design of 10 kW thermoelectric power generation unit for low graded waste heat recovery including a heat storage unit for practical use.

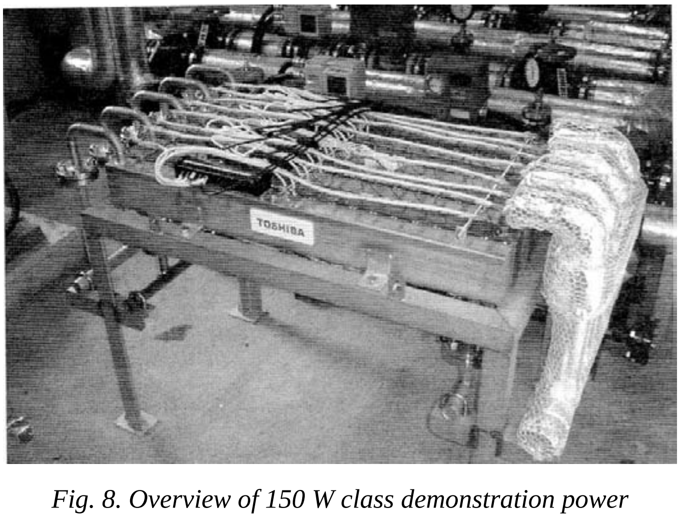

Fig. 8. Overview of 150 W class demonstration power generation system using hot springs.

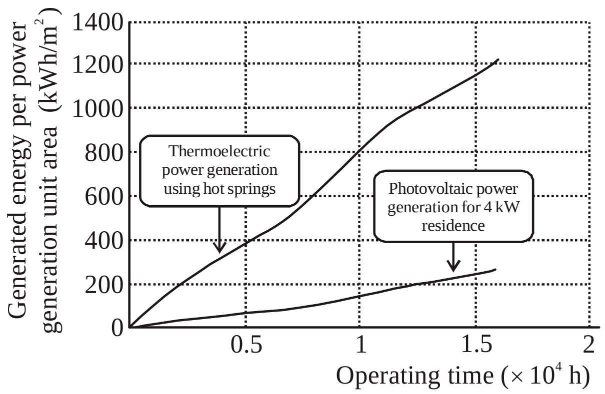

Fig. 9. Comparison of generated energy per unit area for thermoelectric power generation system using hot springs and that for commercial photovoltaic power generation system.

Thermoelectric power generation system using waste heat recovery from motorcycle has been demonstrated by the consortium (Project leader: Prof. Y. Nishino, NIT) of Nagoya Institute of Technology, ATSUMITEC Co., Ltd, AIST and other three companies supported by METI. The surface temperature of motorcycle muffler is about 473 K. Although *Bi-Te* class element is suitable to this temperature range application, in this project Fe_2VAl class Heusler alloy has been selected because of potential supremacy from safety, robustness, resource and cost. At present Fe_2VAl alloy has very high power factor ($S^2\sigma$, S – thermopower, and σ – electrical conductivity) at 300 K, that is, 5.4 mW/m^2·K, but thermal conductivity is very high, that is, 24 W/m·K for *p*-type, and 18 W/m·K for *n*-type respectively. In the project the performance has been improved about 1.5 times due to the reduction of thermal conductivity. Figure 10 shows the power output characteristics for a module of 18 couples based on $Fe_2V_{0.9}Ti_{0.1}Al(p)$ and $Fe_2VAl_{0.9}Si_{0.1}(n)$ elements. The module size is 35 mm×35 mm. The element size is 5 mm^2 × 5 mm. The power output is obtained 0.94 W at 573 K in high temperature. The power density is estimated 0.1 W/cm^2. Figure 11 shows the power generation system of 12 improved modules mounting the surface of motorcycle muffler. The power output is obtained about 12 W at 6 V under the driving condition of 60 km/h to charge a battery. It will be one of the promising applications as the waste heat recovery in the near future.

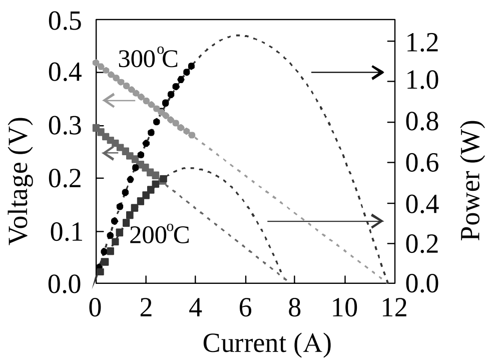

Fig. 10. Power characteristics for a module using Heusler alloy element installed to the muffler of a motor cycle.

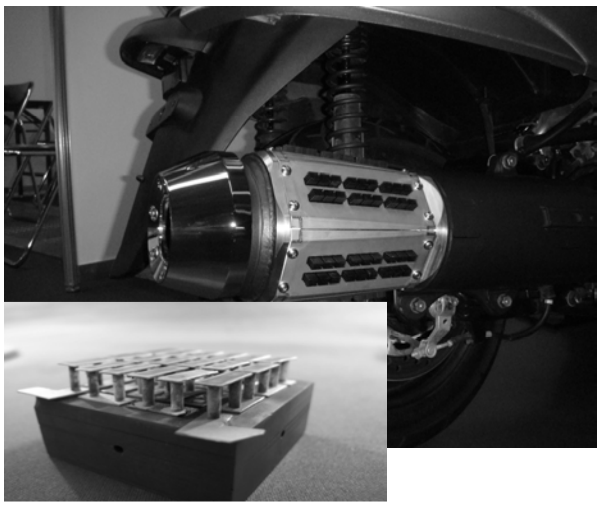

Fig. 11. Thermoelectric power generation module and system mounted on the muffler of a motorcycle.

Progress of thermoelectric material research

In Japan the research on thermoelectric materials has been mainly achieved by universities and national research institutes. The number of members who belong to Thermoelectrics Society of Japan (TSJ) is 340 in 2008. About 54 % of members belong to 65 universities or colleges and 6 national research institutes, which are major leading institutes on science and technology in Japan.

The final goal for thermoelectric material research is an enhancement of thermoelectric performance. Recently in addition to this goal it has been recognized to be important that thermoelectric materials are environmentally friendly, safe, abundant, inexpensive and steady. The research on bulk type materials has been intensively carried out, because in Japan the goal is expected to be applied to more than several kW class power generation systems in waste heat recovery. The research on thin film and low dimensional elements has been also expanded from the view point of scientific interest.

The scientific approaches aiming high performance have been based on so called PGEC (Phonon Glass Electron Crystal) concept. Especially it is very much important to apply nanotechnology to enhance the thermoelectric performance [4], where is a) quantum confinement of electrons to enhance a thermopower, b) low phonon thermal conductivity through structural complexity, and c) substructure approaches which separates the electron crystal from the phonon glass summarized by G. J. Snyder [5]. The researches on layered oxides, Clathrates, composite Skutterdites, half-Heusler compounds, Boron compounds and other various kinds of materials from these aspects have been carried out in Japan, while the researches on *Bi*-*Te* class material and other conventional materials have been also continued. Some topics on the enhancement approaches due to nanostructure for several materials in Japan are introduced as follows:

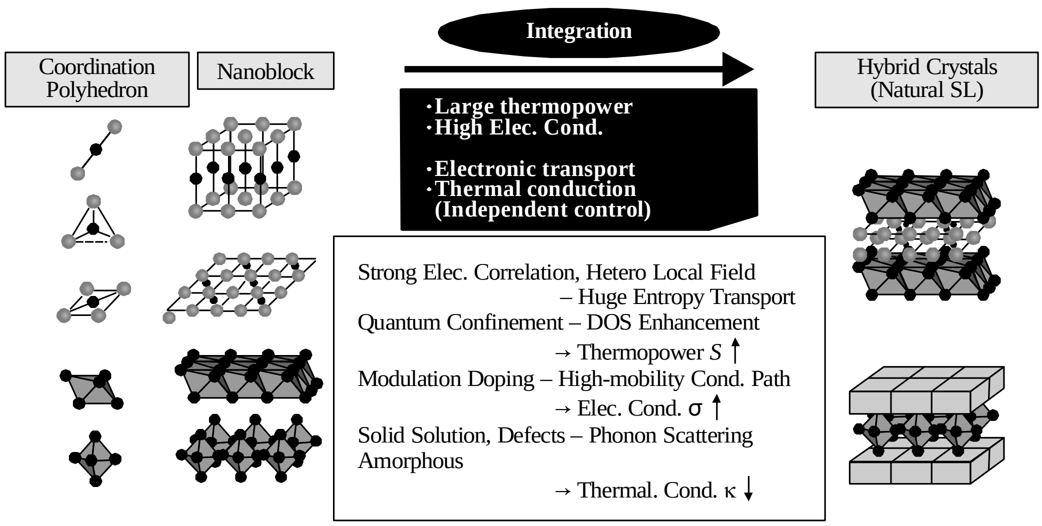

Fig. 12. Concept of nanoblock integration for layered oxides.

Oxides are chemically stable in air even at high temperature and mostly nontoxic. Although oxides have high electric resistivity in general, the layered cobalt oxide such as Na_xCoO_2 was found to exhibit high thermoelectric performance about 12 years ago. Recently a lot of kinds of the layered oxide materials have been investigated. The thermoelectric oxide can be designed by combining a proper nanoblock with another specific nanoblock, so called nanoblock integration as shown in Fig. 12 [3]. It can be also said to be hybrid crystal or natural superlattice that is composed of the periodic arrangement of nanoblock or nanosheet possessing different thermoelectric function such as metallic or insulating. Fig. 13 shows the progress of the top of thermoelectric performance for various kinds of layered oxides. The superlattice structures utilizing undoped $SrTiO_3$ and *Nb* doped $SrTiO_3$(*STO*) were successfully made using Pulse Laser Deposition (PLD) method by H. Ohta et al, so that quantum confinement of electron gas was confirmed to show giant thermopower, resulting in *ZT*=2.4 at 300 K for one unit cell layer of *Nb*-doped *STO* as shown in Fig. 14 [6].

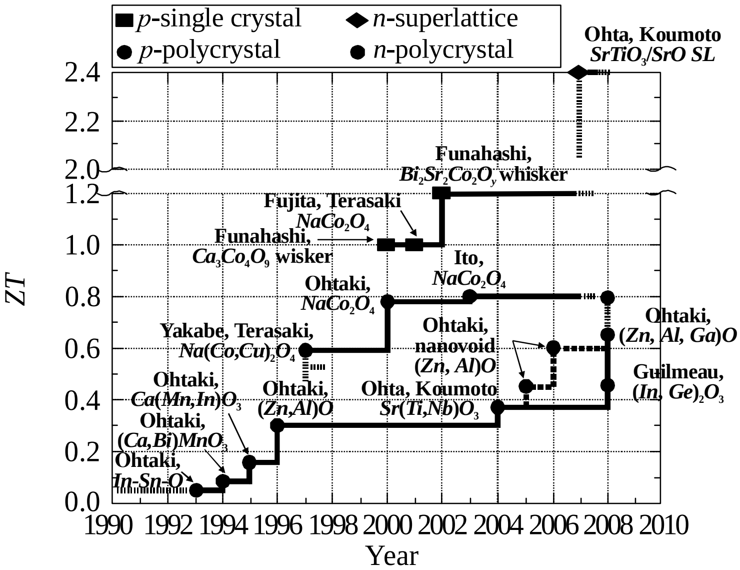

Fig. 13. Progress of dimensionless figure of merit ZT for layered oxide in Japan.

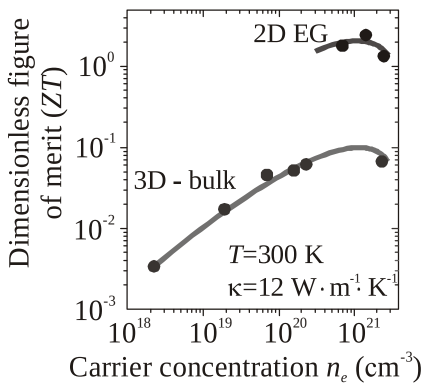

Fig. 14. Performance of a supperlattice layered oxide.

The effect of reduction of thermal conductivity by nanovoid dispersion [7] in sintered *ZnO* has been successfully investigated by H. Ohtaki et al. as shown in Fig. 15. Organic particles (Polymethylmethacrylate) were added as void forming agent (VFA) into the raw powder mixture of *Zn-Al-O*. The sintered samples could show that the electrical conductivity decreased in accordance with the size and amount of VFA, thermopower significantly increased with decreasing the size of VFA and the thermal conductivity reduced by 30% to 35%. Consequently, *ZT* was obtained 0.59 at 1273 K due to the effect of nanovoid forming for *Zn-Al-O* system.

The phase separated nanostructure approach has been investigated to reduce the thermal conductivity for oxides by A. Kosuga et al [8]. Two types of nanorods inside a grain could be formed by the heat treatment of $ZnMnGaO_4$ to $ZnMn_{1.7}Ga_{0.3}O_4$ (tetragonal) and $ZnMn_{0.5}Ga_{1.5}O_4$ (cubic) as intra granular heterogeneous oxides (Intra *GHO*). The thermal conductivity of this intra *GHO* was found to be lower than that of minimum value of the mixture based on a series model. Although the other thermoelectric properties were not satisfactory at present, phase separated nanostructured oxide would be promisingly expected to be applicable to related oxides with high electric properties.

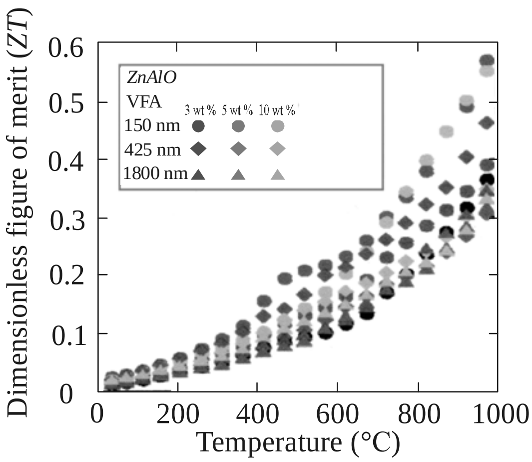

Fig. 15. Effect of nanovoid dispersion to ZT with 3-10% of 150,425,1800 nm VFA.

Half-Heusler compounds have been attracted as environmentally friendly and abundant thermoelectric materials for high and medium range temperature applications. The half-Heulster compounds consist of *ABX*, in which *A* and *B* are typically transition metals and *X* can be *Sn*, *Sb*, *Al*, *Si*, and *Bi*. It is well known that half-Heusler compounds have large power factor ($S^2\sigma$) based on optimizing carrier concentration, while the relatively high thermal conductivity is disadvantageous. The solid solution effect: that is, the differences in atomic mass or size in solid solution can lower the phonon thermal conductivity due to increasing phonon scattering at the interface, is applied to this material system. For half-Heusler ($MA_{0.5}$,$MB_{0.5}$)*NiSn* alloys (*MA*, *MB* = *Hf*, *Zr*, *Ti*) the effect of *M* site substitution on thermoelectric properties has been investigated as *n*-type thermoelectric element by Y. Kimura and H. Ueno [9]. The samples were fabricated with the directional solidification technique to obtain single phase alloys. Temperature dependence of thermal conductivity is shown in Fig. 16, where the carrier contribution to thermal conduction has been proven to be quite small.

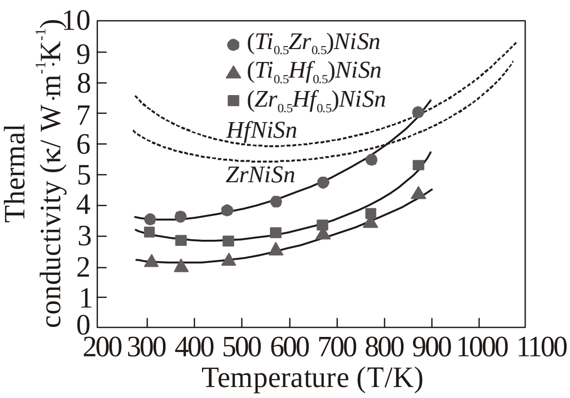

Fig. 16. Temperature dependence of thermal conductivity for n-type half-Heusler ($MA_{0.5}$,$MB_{0.5}$)NiSn system (MA,MB=Hf,Zr,Ti).

Then, the lattice thermal conductivity could be effectively reduced, so that *ZT* was obtained about 0.9 at 900 K. In the experiment they have found the existence of the phase separation nanostructure in (*Ti*, *Hf*)*NiSn* system and (*Ti*, *Zr*)*NiSn* system. They have pointed out that the nanostructure due to phase separation would be mainly caused with the enhancement of performance. The substitution effect on the thermoelectric performance for *p*-type half-Heusler compounds: $ErNi_{1-x}Pd_xSb$ has been studied by K. Kurasaki, S. Yamanaka, et al. [10]. Samples of $ErNi_{1-x}Pd_xSb$ (x = 0.25, 0.5, and 0.75) were prepared by an arc melting technique and long time, high temperature annealing process. Fig. 17 shows temperature dependence of thermal conductivity for $ErNi_{1-x}Pd_xSb$ system, where the thermal conductivity could be substantially reduced by an alloy scattering effect without significant degradation of power factor. At present *ZT* could be about 0.3 at 650 K. In the experiment it is reported that the samples were not completely homogeneous but composed of a few phases such as the matrix phase and impurity phases. According to two independent researches for solid solution of half-Heusler systems, it can be said that a kind of self-assembled nanostructure such as phase separation plays an important role to be effective to the reduction of lattice thermal conductivity insensitive to other electrical properties.

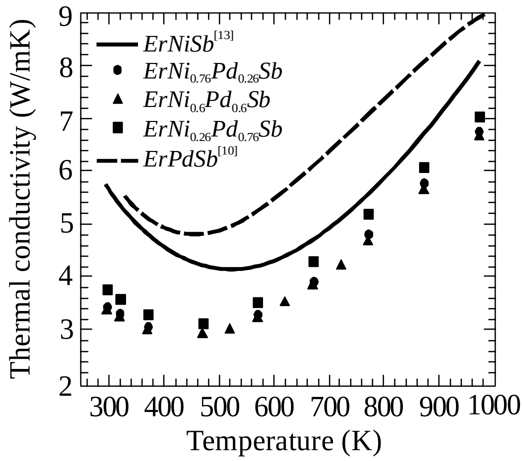

Fig. 17. Temperature dependence of thermal conductivity for p-type half-Heusler $ErNi_{1-x}Pd_xSb$ system.

As for filled skutterudites system, the enhancement of thermoelectric performance has been carried out by means of controlling the microstructure of electroconductive oxide particle in grain size level to increase the phonon scattering at the grain boundaries. The samples of $CeFe_3CoSb_{12}$ filled skutterudite and MoO_2 additive compound have been investigated by S. Katsuyama et al. [11]. $CeFe_3CoSb_{12}$–MoO_2 composite was made by the mechanical alloying and spark plasma sintering techniques. The thermopower is reduced by the formation of composite with MoO_2, while the electrical resistivity and thermal conductivity are also reduced. Temperature dependence of *ZT* for composite filled skutterudite $(CeFe_3CoSb_{12})_{1-x}(MoO_2)_x$ as a function of *x* is shown in Fig. 18.

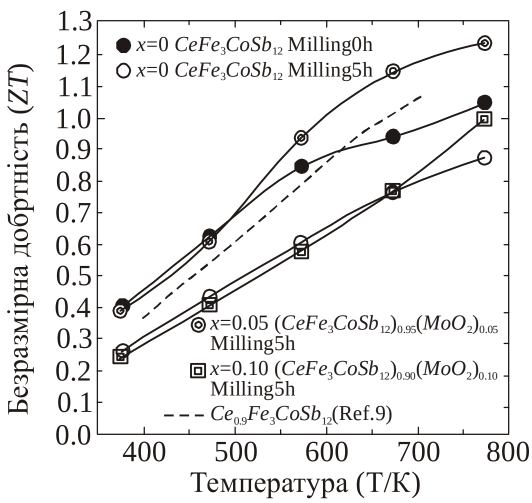

Fig. 18. Temperature dependence of dimensionless figure of merit ZT for filled skutterdite $CeFe_3CoSb$ and MoO_2 additive compound.

As a result, the maximum *ZT* was obtained 1.22 at 773 K. The formation of the composite with electroconductive oxide particles shows effective in enhancing the thermoelectric performance for filled skutterdites system. It can be suggested that the formation of nanoscale structured composite would be more effective.

Future Prospects

It is necessary and urgent to propagate that the thermoelectric power generation technology is good for the society. At present it is very good chance to let the public know that the thermoelectric power generation technology can contribute to the solutions of environmental issues, as the public has highly concerned with the environmental conservation. Therefore, the above-mentioned demonstration experiments for long run will play an important role for the popularization of thermoelectric power generation technology. At this stage the sample supply of the advanced thermoelectric power generation modules and small scale systems are very much important to be confirmed the thermoelectric performance by the users. The small scale production line of the advanced *Bi-Te* based modules developed in the national project will be provided with few companies [12]. The peculiar points of these modules are surely 1) high efficiency, 2) high temperature use up to 553K, 3) high power density more than 1.0 W/cm^2, and 4) large power output or high voltage per module in consideration with the adaptation in utility environment.

The near-term application to be commercialized would be a waste heat recovery system from industrial and private sectors in consideration for our immediate needs. In the future the major application in the society will be the waste heat recovery from transportation sector.

As for the materials research the seeds of innovative thermoelectric material systems have existed for vast scientific and engineering fields. It can be said that we have just found the entrance of the thermoelectric innovation. It is sure that one of the key words is nanostructure. It is urgent for us to boost further the advanced material research and development under the leadership of METI and NEDO as a national project.

Concluding remarks

Based on the developed results in the national project for the advanced thermoelectric power generation systems and some practical experiences of small scale experiments on several application systems for the waste heat recovery from industrial and private sectors, the progressing activities aiming to proceed to the commercialization phase has been carried out by several private companies. The effort has been intensively achieved step by step for the establishment of thermoelectric power generation technology for practical use.

The final goal for thermoelectric material research is an enhancement of thermoelectric performance. Recently it has been also recognized to be important that thermoelectric materials are environmentally friendly, safe, abundant, inexpensive and steady. The research on bulk type materials has been intensively carried out in Japan, because first of all the goal is expected to be applied to more than several kW class power generation systems in waste heat recovery. It is sure that the nanotechnology in thermoelectric materials has played an important role to the enhancement of thermoelectric performance.

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