

Research on Skutterudite-type Thermoelectric Materials for On-board Waste Heat Recovery System

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ABSTRACT

Skutterudite-type thermoelectric materials were researched with the goals of enhancing the performance of a lightweight and compact thermoelectric waste heat recovery system and scaling-up to mass production. Measures such as reducing the starting material cost and purity and increasing the manufacturing process yield were promoted, and prospects were achieved for mass production scale manufacturing of high performance thermoelectric materials (P-type thermoelectric properties $ZT > 0.8$, N-type thermoelectric properties $ZT > 1$) at approximately 1/100 the current proto-type manufacturing cost. Material nano-structuring was performed to enhance the properties, and the results showed that rare-earth metals added to skutterudite-type thermoelectric materials oxidize easily, and that the carrier concentration in the materials changes due to this oxidation, which has an acute effect on the thermoelectric characteristics. The effects of material nano-structuring in an environment that suppresses oxidation and adjustment of the carrier concentration enhanced the thermoelectric properties by 23.8%.

1. Introduction

Fuel economy regulations aimed at reducing CO₂ emissions are increasing in number and severity around the world, and further reduction of vehicle energy loss is demanded. The energy balance of a typical gasoline fuel automobile is such that only approximately 25% of the total energy is used as running energy, approximately 40% is discarded as exhaust gas, and approximately 30% is discarded as waste heat for purposes of engine cooling⁽¹⁾. Waste heat utilization technology that effectively uses this discarded heat will play an important role in future enhancement of vehicle fuel economy. In particular, technology that regenerates waste heat into electricity is attracting attention as an important technical development item in consideration of future motorization.

There are a number of methods for regenerating waste heat into electricity. Examples include an on-board Rankine cycle⁽²⁾ and an on-board Stirling engine⁽³⁾, but these systems have complex structures that are large and heavy, so practical application has not been achieved. In contrast, regarding waste heat recovery technology that

uses thermoelectric conversion, Honda has previously reported the verification results of a lightweight and compact thermoelectric system concept with a characteristic vacuum structure⁽⁴⁾. In addition, many automobile makers are also working to develop such a system⁽⁵⁾⁻⁽⁹⁾. However, the thermoelectric materials used in recovery systems that use thermoelectric conversion typically have lower conversion efficiency compared to other waste heat recovery methods⁽¹⁰⁾, and this is thought to be a factor delaying commercialization of these systems. In addition, a lightweight and compact system design and assembly technology that includes modularization are needed to create a thermoelectric conversion system that is suitable for mass production. Moreover, thermoelectric material development to enhance properties and scale-up production, and system integration that takes into account the energy balance of a vehicle are also important. Furthermore, there are various development issues such as the need to secure durability and reliability. This paper focuses in particular on thermoelectric material development among these various issues.

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2. Overview of Thermoelectric Material Research

When a temperature difference is applied to a material, an electromotive force is generated due to the Seebeck effect. Materials for which this effect is particularly pronounced are called thermoelectric materials. Thermoelectric materials include P-type materials in which electricity flows from the hot side to the cold side, and N-type materials in which electricity flows from the cold side to the hot side. Electric power regeneration can be achieved by connecting thermoelectric materials in series via electrodes. The basic concept of an on-board thermoelectric conversion system is a structure that generates electric power by using the high temperature waste heat from the exhaust gas and the coolant used for engine cooling to apply a temperature difference to thermoelectric materials.

Equation (1) below expresses the energy conversion efficiency η for regenerating input heat energy into electricity.

$$\eta = \left(\frac{T_h - T_c}{T_h} \right) \left(\frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_c/T_h} \right) \quad (1)$$

Here, T_h (K) is the temperature on the hot side and T_c (K) is the temperature on the cold side of the thermoelectric element. ZT is expressed by Eq. (2) below as a figure of merit that indicates the thermoelectric material properties.

$$ZT = \left(S^2 \sigma / \kappa \right) T \quad (2)$$

Here, S is the Seebeck coefficient, σ is the electric conductivity, and κ is the thermal conductivity. In addition, κ can be expressed as follows by the carrier thermal conductivity κ_c , which uses carriers such as electrons and holes as thermal energy propagators, and the lattice thermal conductivity κ_{ph} , which uses phonons, or lattice vibration, as energy propagators.

$$\kappa = \kappa_c + \kappa_{ph} \quad (3)$$

From Eq. (2) and Eq. (3), the thermoelectric material ZT is expressed as follows.

$$ZT = \left[S^2 \sigma / (\kappa_c + \kappa_{ph}) \right] T \quad (4)$$

Enhancement of ZT involves increasing the numerator $S^2 \sigma$, which is called the power factor (PF) or reducing the denominator $\kappa_c + \kappa_{ph}$ in Eq. (4). However, S , σ and κ_c are all physical property values derived from the carrier conduction, so for example, increasing the numerator induces an increase in the denominator. This complex interrelation makes it a challenge to simply enhance

ZT . In contrast, κ_{ph} is an independent parameter derived from phonon propagation, so methods that reduce κ_{ph} are typically used as the thermoelectric material design method. As a concrete example of such a method, B. Poudel et al. performed dry mechanical milling on BiTe-type thermoelectric material powder and then used the spark plasma sintering method to manufacture a nano-structured sintered compact. The results showed that thermoelectric properties can be enhanced by reducing $\kappa_{ph}^{(11)}$, and since then there have been many reports of research on nano-structured thermoelectric materials.

This development targeted gasoline vehicles, and focused on skutterudite-type thermoelectric materials which, among materials suited to the waste heat recovery temperature of a gasoline vehicle, are inexpensive, high performance, and do not contain harmful elements. MX_3 compounds ($M = Co, Rh, Ir; X = P, As, Sb$) have a skutterudite-type crystal structure, and $CoSb_3$ in particular is known to exhibit thermoelectric characteristics (Fig. 1). In addition, the $RM'_4X'_{12}$ ($R = La, Ce, Eu, Yb; M' = Co, Fe; X' = Sb$) with the atoms filled in the cage part in the figure reduces κ_{ph} through a special lattice vibration called a rattling effect, so it is known to exhibit high thermoelectric properties in the medium to high temperature range⁽¹²⁾. The yellow, green and blue atoms in the figure indicate Sb, M' and R , respectively.

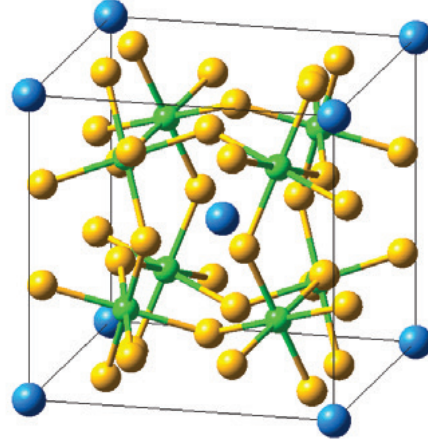


Fig. 1 Schematic illustration of skutterudite-type crystal structure

3. Research Goals

Most thermoelectric materials thus far, including skutterudite-type thermoelectric materials, have been small-scale synthesized materials on the level of several tens of grams, such as those described in academic papers, and these have all been synthesized using high-purity reagents. As mentioned above, thermoelectric-based waste heat recovery technology has not yet been used for mass

production by any automobile maker, so of course mass production technology for these materials also has not been established. Therefore, this development first considered the purity of the starting materials that can actually be obtained from suppliers, set a tentative target value of 50 million $2 \times 2 \times 2$ -mm thermoelectric elements per year (equivalent to an annual production scale of 3000 kg), and verified a manufacturing process that enables mass production. Depending on the amount of thermoelectric materials used in the thermoelectric generation system, this target quantity is enough to support a production scale of approximately 100,000 units/vehicles per year. In addition, approaches have also been reported for enhancing the properties of skutterudite-type thermoelectric materials using the abovementioned nano-structuring, but these studies have all been limited to small scale (laboratory scale) verification^{(13), (14)}. As mentioned above, low conversion efficiency is an issue for on-board thermoelectric waste heat recovery systems, so the effects of nano-structuring on the developed material were confirmed and analyzed in detail in consideration of mass production scale manufacturing.

4. Mass Production Scale Manufacturing of Thermoelectric Materials

The thermoelectric material manufacturing process begins from selection of the starting materials, and proceeds through the dissolution synthesis, homogenization, powderization, sintering, and dicing processes. Laboratory scale synthesis consists of encapsulating high-purity reagents as the starting materials in an ampule-type quartz tube and performing melting heat treatment. However, mass productivity was taken into account, and the manufacturing process for the developed material was streamlined by applying gas-atomization in place of synthesis, homogenization, and powderization.

The starting materials assumed for mass production contain various impurities, so the influence of these impurities was confirmed. A slight drop in performance was observed when the high-purity reagents were replaced with starting materials that contain impurities, but the performance was restored for the most part by finely adjusting the material composition again (Fig. 2).

Granulation used gas-atomization as mentioned above, and this enabled the suppression of the effects of inter-lot variance (composition changes) during material synthesis, which is unavoidable with small-lot manufacture. When synthesis is performed by gas-atomization, a powder grain size distribution exists. Therefore, the influence of powder grain size on performance was confirmed. The results showed that when powder with a grain size of 20 μm or less is used, the oxygen concentration increases and the thermoelectric material properties drop compared to when using powder with a larger grain size (Fig. 3). The reason for this drop in conversion efficiency when

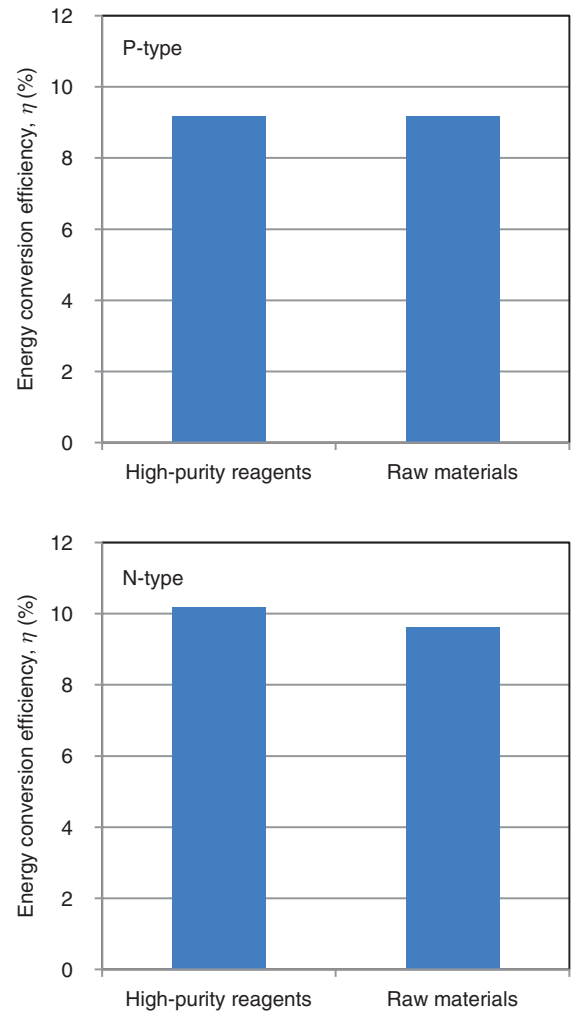


Fig. 2 Thermoelectric performance versus purity of starting materials for using gas-atomization

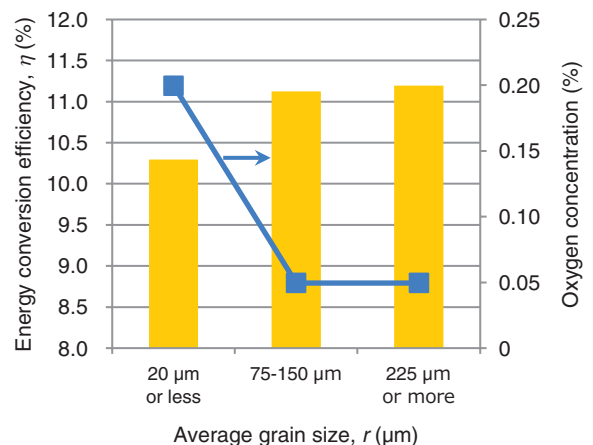


Fig. 3 Thermoelectric performance and oxygen concentration versus gas-atomized powder radius

the oxygen concentration increases is described in the following section. Much powder with a grain size of 20 μm or less was present in the initial manufacturing process condition, but subsequent optimization of the manufacturing process parameters, such as the injection pressure and nozzle hole diameter, enabled us to reduce the amount of powder with a grain size of 20 μm or less.

To enhance the tact time in the next process, sintered compact manufacture, it is necessary to increase the diameter of the sintered compact. Here, the key is how to realize the manufacture of homogeneous sintered compact with a large diameter. Uneven firing of the sintered compact becomes an issue as the diameter increases, so it is important to ascertain the maximum sintered compact size that can be homogeneously fired. This development established technology for manufacturing a $\phi 200$ sintered compact using the spark plasma sintering method. It was assumed that nano-structured powder would be sintered as described in the following section, so the spark plasma sintering method was selected to enable quick sintering in a short time so that as little grain growth as possible occurred in the nano-structured powder during the sintering heat treatment. Figure 4 shows the results of evaluating the

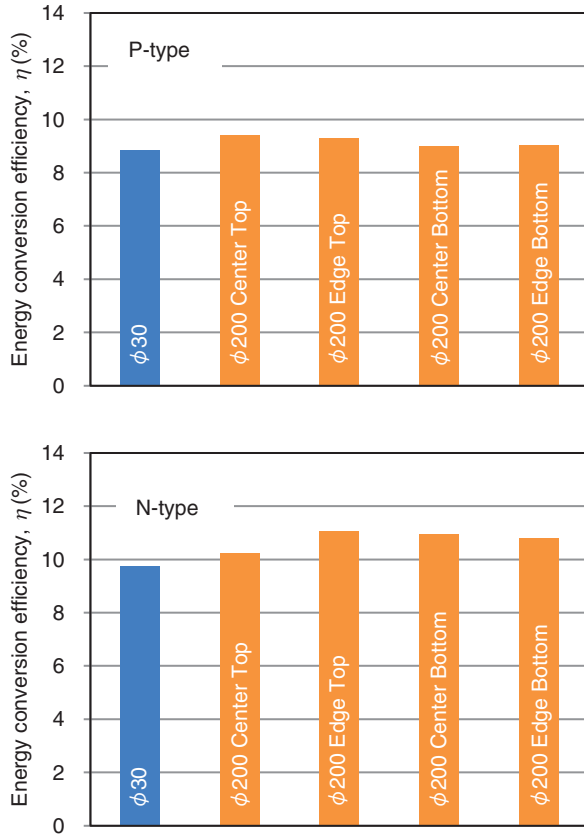


Fig. 4 Energy conversion efficiency of P-type and N-type sintered skutterudite thermoelectric materials 200 mm in diameter

thermoelectric properties at various locations of the sintered compacts. There was little or no difference in properties at any of the locations, indicating that good, homogeneous sintered compacts can be manufactured.

This series of thermoelectric material developments enabled scale-up manufacture of a thermoelectric material with thermoelectric properties that exceed those of a $\phi 30$ sintered compact, as shown in Fig. 5. The main factor enhancing performance was a vast reduction in the amount of powder used that had a grain size of 20 μm or smaller (Fig. 3). The obtained sintered compact was sliced, polished and then diced to create thermoelectric elements with a square pillar shape, and it was verified that the material can be processed to a size with a cross-sectional area of 1 mm $\times$ 1 mm. When this manufacturing process is used to produce the tentative target quantity of material, the effects of reducing the starting material cost, increasing the yield, and economies of scale due to mass production enabled us to lower the cost to approximately 1/100 that of the materials supplied as a prototype.

When this new thermoelectric element is installed in the thermoelectric generation system currently being developed, and the US 5 cycle (U.S. automobile fuel economy labeling method) driving mode average value is estimated through the method used in past studies⁽⁴⁾, a fuel economy enhancement effect of approximately 1% can be expected for the system with the greatest cost-effectiveness, including the early warming effect during engine start. In addition, enhancing the input heat amount, the heat transfer efficiency, and other thermoelectric system properties can further increase the waste heat recovery performance. Effects can also be anticipated such as the use of waste heat to supply the power consumed by always-on sensors, for which demand is expected to increase due to self-driving and other applications in the future.

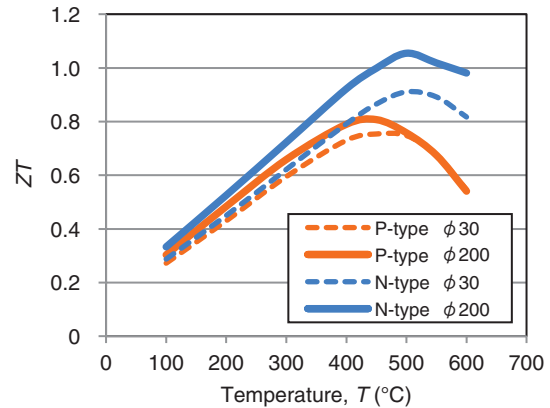


Fig. 5 Resultant ZT properties for developed skutterudite thermoelectric materials that can be mass produced

5. Enhancement of Properties by Material Nano-structuring

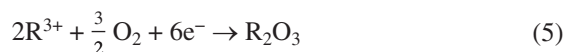
Gas-atomization was used to prepare several kg of N-type skutterudite-type thermoelectric materials with rare-earth metals added, and then a planetary ball-mill was used to perform nano-structuring.

Figure 6 shows electron back scatter diffraction (EBSD) images of the material structure before and after ball-milling. The average crystal grain size of the gas-atomized powder is approximately 15 μm , and the average crystal size after nano-structuring is approximately 300 nm. This shows that pulverization by a planetary ball-mill produces a nano-structure with a grain size approximately 1/50 and a grain volume approximately 1/125000 those of gas-atomized powder.

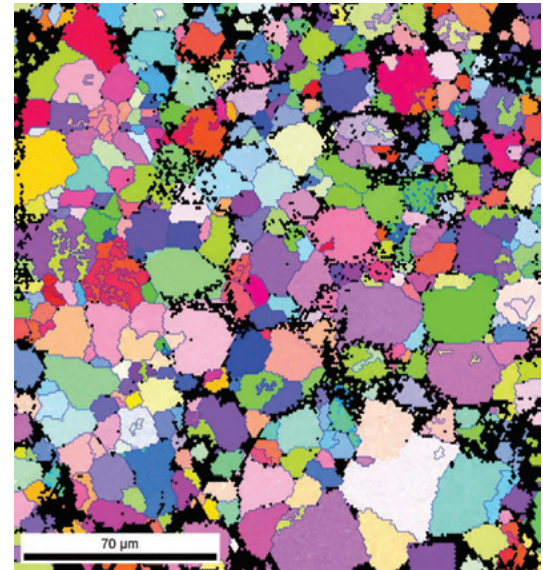
Figure 7 shows the temperature dependence of each physical property value that characterizes the thermoelectric properties indicated by Eq. (4). The primary goal of nano-structuring is to reduce only κ_{ph} and enhance performance. However, physical property values other than κ_{ph} also change before and after nano-structuring, such as for example the change in σ shown in Fig. 7(a). The two likely factors behind this drop in σ are thought to be the effect of the inhibition of electrical conduction by nano-structuring and the effect of the change in the carrier concentration. Regarding the effects of nano-structuring, Fig. 8 shows the test results of σ dependency on crystal grain size for different milling conditions. Ball-milling greatly reduced σ , but no clear dependency of the milled material σ on the crystal grain size was observed thereafter.

Regarding the influence of the change in carrier concentration, the oxygen concentration was confirmed to increase by 0.18 wt%O as shown in Table 1. The tests were performed using a controlled atmosphere glove box or similar facility, but this increase is thought to be due to oxidation by residual oxygen that could not be removed. The material structure was observed using transmission electron microscopy (TEM) and energy dispersive X-ray spectrometry (EDX) to confirm the oxide format. The results showed that rare-earth oxides had formed in the materials and were unevenly distributed along the crystal grain boundaries as shown by a, b and c in the figure (Fig. 9 and Table 2).

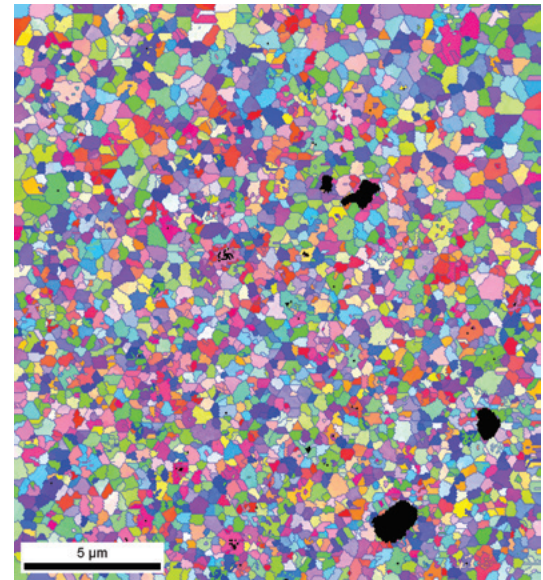
The rare earth oxidation reaction is expressed by the following equation.



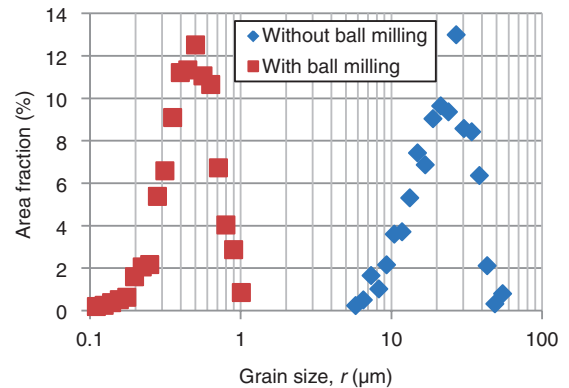
This reaction equation (5) shows that electrons are consumed when rare-earth oxides are generated. This material is an N-type material, so when electrons are consumed, the carrier concentration in the material decreases, or in other words, σ drops. This is presumed to be the reason for the drop in σ shown in Fig. 7(a).



(a) EBSD images without ball-milled material



(b) EBSD images with ball-milled material



(c) Grain size distribution

Fig. 6 EBSD images of N-type skutterudite thermoelectric materials, and resultant grain size

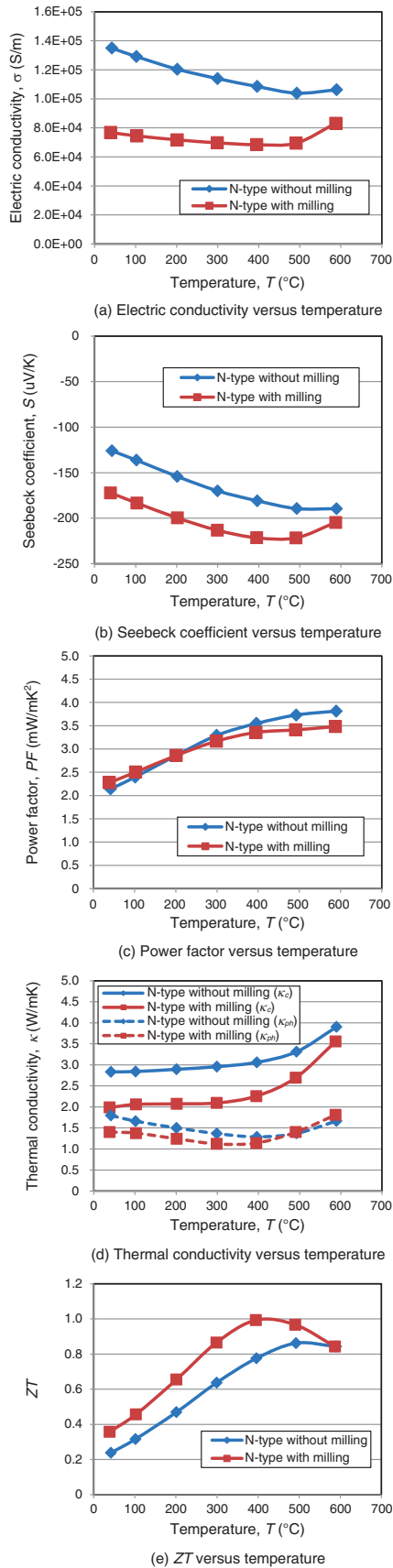


Fig. 7 Temperature dependence of thermoelectric properties derived from ball-milling process

Table 1 Oxygen concentration of thermoelectric materials before and after ball-milling treatment

	Before milling	After milling
Oxide content	0.14	0.32

(wt%O)

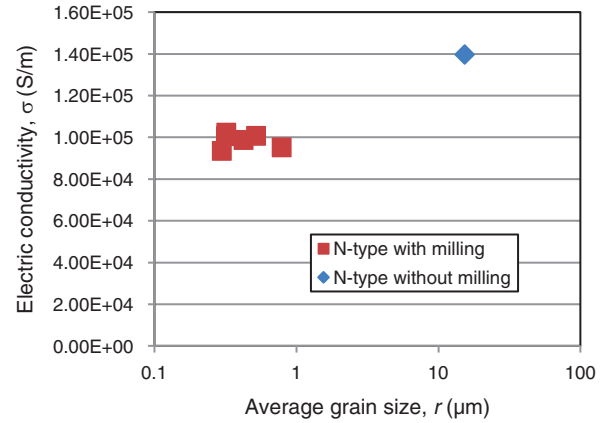


Fig. 8 Electric conductivity versus average grain size at RT. Except for the data with an average grain size of 15.28 μm , the other data were derived after several ball-milling processes

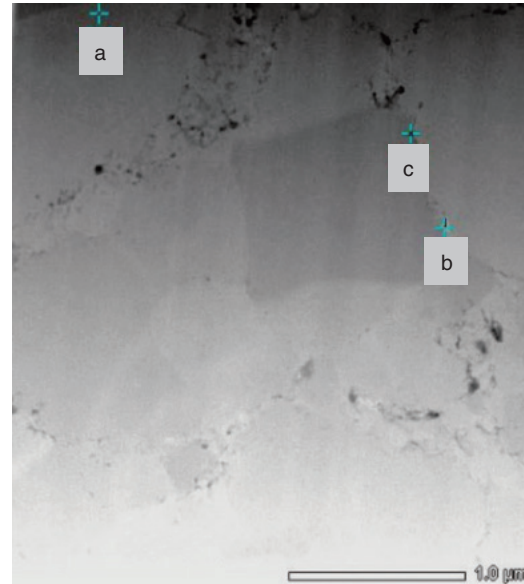


Fig. 9 TEM image of ball-milled materials microstructure

Table 2 Chemical composition analysis results for each point derived by EDX equipped with TEM

Point	O	Yb	Fe+Co	Sb	Others
a	0.8	0.8	34.3	63.1	Bal.
b	31.1	23.9	17.8	27.2	Bal.
c	19.3	2.8	21.9	44.9	Bal.

(atom%)

Equation (4) shows that ZT decreases when only σ drops, but the absolute value of S increases after ball-milling as shown in Fig. 7(b), so as a result $S^2\sigma$ is maintained [Fig. 7(c)]. Material general theory holds that as the carrier concentration in the materials increases, σ increases and S decreases, so $S^2\sigma$ indicates a certain maximum carrier concentration value⁽¹⁵⁾. The results of this development are thought to be that because while the carrier concentration changed, it remained within the ideal $S^2\sigma$ range. However, according to the Wiedemann-Franz law ($\kappa_c/\sigma = LT$: L = Lorentz number, T = temperature), σ and κ_c have a proportional relationship. This means that a drop in σ results in a reduction in κ_c , so ZT increases according to Eq. (4). Therefore, the change in the carrier concentration due to this process has the overall effect of increasing ZT .

Next, κ_{ph} was examined. When performing material design of thermoelectric materials, it is important to reduce κ_{ph} as mentioned above, and the two methods of adding rare-earth metals (La, Yb, Ce, etc.) and material nano-structuring are used for skutterudite-type thermoelectric materials. Rare-earth metals are added to induce special lattice vibration to produce a rattling effect that reduces κ_{ph} . However, as the materials oxidize, the added rare-earth metals form oxides, so the amount of added rare-earth metals in the material lattice decreases and κ_{ph} increases. In contrast, nano-structuring reduces κ_{ph} , so the balance between rare-earth metal addition and material nano-structuring determines the amount of increase or decrease in κ_{ph} . The temperature dependence of κ_{ph} shown in Fig. 7(d) indicates that κ_{ph} decreases after milling as a result of both of these methods. This indicates that the effect of material nano-structuring exceeds the increase in κ_{ph} due to rare-earth oxide formation.

These results show that when nano-structuring is performed on skutterudite-type thermoelectric materials, κ_{ph} is reduced as initially intended, and the thermoelectric properties ZT are also enhanced as shown in Fig. 7(e) as a compound effect of κ_c also decreasing. Here, the ZT area value increased by 23.8% (11.3% in terms of energy conversion efficiency) over the range from 100°C to 600°C. Scale-up of this nano-structuring is currently being investigated.

6. Conclusion

This paper reported an approach to creation of a manufacturing process that enables mass production of skutterudite-type thermoelectric materials for an on-board thermoelectric waste heat recovery system. This research achieved prospects for creating a material manufacturing process with an annual production scale of 100,000 units/vehicles that enables a reduction in the manufacturing cost to approximately 1/100 the prototype cost. In addition, nano-structuring was performed on skutterudite-type thermoelectric materials in consideration of mass production scale manufacturing, and the results showed that the effects

of nano-structuring and changing the carrier concentration enhanced the thermoelectric properties by 23.8%.

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