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Power Generation Characteristics of Mg_2Si Uni-Leg Thermoelectric Generator

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Mg_2Si thermoelectric (TE) elements were fabricated by a plasma-activated sintering method using a commercial polycrystalline *n*-type Mg_2Si source produced by the Union Material Co., Ltd. This material typically has a *ZT* value of ~0.6. A monobloc plasma-activated sintering technique was used to form Ni electrodes on the TE elements. The dimensions of a single element were 4.0 mm × 4.0 mm × 10 mm, and these were used to construct a TE module comprising nine elements connected in series. To reduce the electrical and thermal contact resistance of the module, each part of the module, i.e., the elements, terminals, and insulating plates, was joined using a Ag-based brazing alloy. In addition, to maintain the temperature difference between the top and bottom of the module, a thermal insulation board was installed in it. The observed values of open-circuit voltage (V_{OC}) and output power (P) of a uni-leg structure module were 594 mV and 543 mW, respectively, at a maximum $\Delta T = 500$ K.

Key words: Mg_2Si, thermoelectric, module, uni-leg, plasma-activated sintering, silicide

INTRODUCTION

The relentless increase in the concentration of atmospheric CO_2 due to the increase in energy generation using fossil fuels is accelerating global warming. As a measure to prevent global warming, improving the energy conversion efficiency of energy generation systems using fossil fuels is important.

Thermal-to-electric energy conversion from waste heat sources is a viable technology that can be instrumental in improving the potential energy conversion efficiency of caloric power generation, such as conventional heat engines and industrial furnaces. For practical use of these middle- to high-temperature waste recovery systems that are not covered by the Bi-Te system, the development of TE modules that can be used in the middle to high temperature range is indispensable. Magnesium silicide (Mg_2Si) has been identified as a promising advanced thermoelectric material, operating at temperatures ranging from 500 K to 800 K.[1–3] The dimensionless figure of merit, *ZT*, characterizing the efficiency of a TE material, for Mg_2Si grown using the vertical Bridgman (VB) method has already reached 1.1, while that for Mg_2Si sintered using the plasma-activated sintering (PAS) technique has reached 0.6 to 0.8, and each of these has the necessary performance for practical use.[4–6] Additionally, Mg_2Si is a sustainable and safe material because its constituent elements are abundant in the Earth's crust and its processing byproducts are nontoxic. However, even though a large number of studies have been done on the TE properties of Mg_2Si,[7–12] the output characteristics of Mg_2Si TE elements and modules have not been sufficiently investigated.

Here we report on the power generation characteristics of a uni-leg structure[13,14] TE module using *n*-type Mg_2Si elements. In this work, although the *ZT* value of sintered Mg_2Si is lower than that of grown Mg_2Si, we have used sintered Mg_2Si for the

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fabrication of the TE elements. The reason for this is that, from a practical viewpoint, such as the time needed to fabricate them and the cost of the process, the sintering process is better than the VB method at present. In terms of the fabrication of the TE elements, to form a good contact between the element and the metal parts in the module, we formed Ni electrodes on the Mg_2Si by employing a monobloc PAS technique. The Ni electrodes can also play an important role in the prevention of diffusion of Ag brazing alloy, which is used as a connecting medium. Prior to this research, as reported by Oguni et al.,[15] attempts were made to deposit Cu, Ti, and Ni electrodes on Mg_2Si by employing the same process used in this experiment. However, it appears that Cu and Ti are unstable in our process. Therefore, we used Ni for the electrode material in this work. Using this Mg_2Si element with Ni electrodes, we fabricated a uni-leg TE module comprising only *n*-type Mg_2Si. Compared with the conventional Π structure TE module, the uni-leg structure reduces the problems associated with thermal expansion differences between *p*- and *n*-type TE elements, and as a result, this architecture contributes to increased reliability of the TE module. Additionally, the uni-leg structure greatly simplifies the construction of the module and consequently reduces the cost of the product, because measures against thermal expansion differences between *p*- and *n*-type TE elements are not needed for this architecture.

EXPERIMENTAL PROCEDURES

The starting material for the fabrication of the Mg_2Si TE devices was presynthesized commercial polycrystalline Al-doped Mg_2Si supplied by Union Material. This presynthesized Mg_2Si was prepared from a mixture containing granular Mg (99.95%) and powdered Si (99.99999%), in stoichiometric ratio of 2:1, and was synthesized in an electric furnace. The polycrystalline Mg_2Si was ground into powder with particle size of 75 μm or less. The Mg_2Si powder was then placed into a carbon die sandwiched between Ni powder layers and sintered using an Elenix PAS-III-Es employing a monobloc plasma-activated sintering (PAS) technique. For the PAS method, the powders were processed at 1073 K for 2 min at pressure of 29.4 MPa in Ar (0.06 MPa) atmosphere. The dimensions of the sintered billet were 15 mm diameter and 10 mm thickness. The sintered billets were then cut using a wire saw. The shape of the fabricated element is shown in Fig. 1. The dimensions of the elements used for the module were 4 mm × 4 mm × 10 mm, including the Ni electrodes, and the thickness of Ni electrodes was 0.2 mm. The Ni layer thickness was controlled by controlling the amount of powder. The uni-leg TE module was fabricated using nine elements, each of which was connected electrically in series using Ni terminals. As shown in Fig. 2, the Ni terminals connect the hot side of one element with the cold side of its neighboring element. The elements and Ni terminals were joined using Ag-based brazing alloy. Al_2O_3 plates, with dimensions of 28 mm × 28 mm × 1.0 mm, were used for the electrical insulating plates. TE elements and Ni terminals, with area of 20 mm × 20 mm, were placed between two Al_2O_3 plates. The calculated occupancy rate of the elements in the module based on the area of the elements was 36%. In addition, to maintain the temperature difference between the top and bottom of the module, a thermal insulation board was installed in it. A photograph of the fabricated Mg_2Si uni-leg module is shown in Fig. 3.

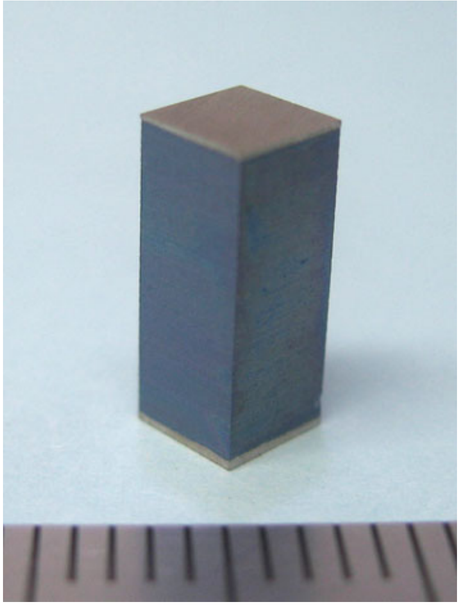

Fig. 1. Photograph of Mg_2Si TE element with Ni electrodes.

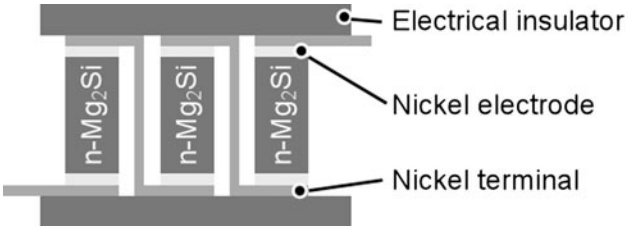

Fig. 2. A schematic diagram of the uni-leg structure TE module.

The Seebeck coefficient (S) and the electrical resistivity (ρ) of the source material were measured over the temperature range from 350 K to 860 K using Ulvac-Riko ZEM-2 equipment. The thermal conductivity (κ) was measured over the temperature range from 300 K to 873 K, employing a laser flash method, using a Ulvac-Riko TC-7000H. The electrical resistance at room temperature of the elements and module were measured using an Adex AX-222. The open-circuit voltage and thermoelectric power output with the temperature difference, ΔT, ranging from 100 K to 500 K, were measured in air using a Union Material UMTE-1000 M. The top of the element or module was heated by an electrically heated stainless-steel block, whereas the base was cooled with an aluminum block. Heat to the heating block was provided by an electrical heater at 473 K to 873 K, whereas the cooling block was maintained at 373 K by a combination of water cooling and electrical heating. The output voltage, output current, and output power were measured under closed-circuit conditions, varying the value of the external load using an Adcmd 6242.

RESULTS AND DISCUSSION

Table I presents the TE properties of the source material used in the fabrication of the Mg_2Si TE elements. The performance of TE materials depends on the dimensionless figure of merit $ZT = S^2T/\rho\kappa$, where T, S, ρ, and κ are the absolute temperature, Seebeck coefficient, electrical resistivity, and thermal conductivity, respectively. The observed S values were negative for the measured sample, indicating n-type conductivity. The ZT value increased with increasing temperature, and the maximum ZT value was 0.62 at 873 K.

Figure 4 shows the I–V characteristics and output power of a single element with respect to temperature difference, ΔT, ranging from 100 K to 500 K. The dimensions of the measured element were 4 mm × 4 mm × 10 mm, including the Ni electrodes. The heater block was heated at 473 K to 873 K, whereas the cooling block was maintained at 373 K. The measured open-circuit voltage, V_{OC}, of the element was 45.4 mV at ΔT = 300 K, 70 mV at ΔT = 400 K, and 92 mV at ΔT = 500 K. When compared with the expected V_{OC} value, the measured V_{OC} value is lower. This decrease in the V_{OC} value occurs because there is a deviation between the measured temperature and the temperatures at the bottom and the top of the element, since we measured the temperature of the heater block and the cooling block, respectively. The measured maximum output power ($P_{\max}$) with a load resistance was 39.5 mW (1754 mA, 22.5 mV) at ΔT = 300 K, 74.6 mW (2132 mA, 35 mV) at ΔT = 400 K, and 121 mW (2623 mA, 46 mV) at ΔT = 500 K. The estimated output power density of a single element at ΔT = 500 K was 7.6 mW/mm^2. Although the estimated output power density showed good performance, there is room for improvement in this element. This is because the measured electrical resistance at room temperature of a single element was 6.2 mΩ, while the calculated electrical resistance value using the measured electrical resistivity at room temperature of the source Mg_2Si material of 6.54×10^{-6} Ωm is 3.86 mΩ. The MF value, which is an index of the quality of the element, defined as MF = $R_{\mathrm{ideal}}/R_{\mathrm{int}}$, where R_{ideal} is the theoretical

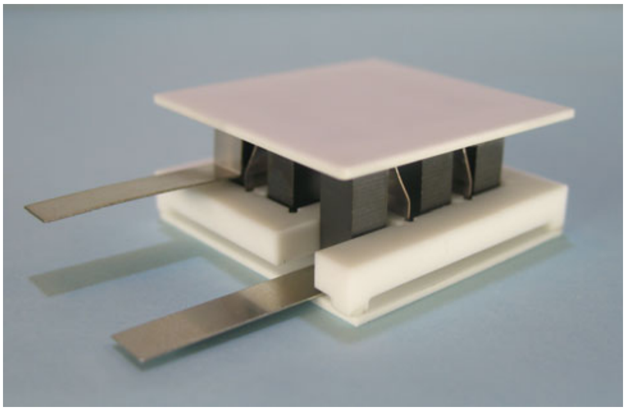

Fig. 3. Photograph of the uni-leg TE module, consisting of 9 TE elements.

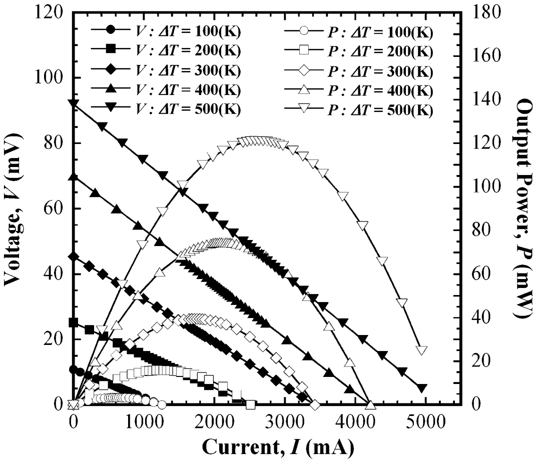

Fig. 4. The results of the I–V characteristics and the output power measurement with a load resistance for a single element with various temperature differences, ΔT, ranging from 100 K to 500 K.

Table I. Thermoelectric Properties of Source Mg_2Si Material

Temperature (K)	Seebeck Coefficient (μV/K)	Electrical Resistivity (Ωm)	Thermal Conductivity (W/mK)	Dimensionless Figure of Merit
373	−154.7	8.79×10^{-6}	6.73	0.15
473	−173.5	1.16×10^{-5}	5.09	0.24
573	−218.4	1.87×10^{-5}	4.28	0.34
673	−257.7	2.92×10^{-5}	3.75	0.41
773	−249.0	2.51×10^{-5}	3.44	0.56
873	−254.5	2.82×10^{-5}	3.27	0.62

resistance and R_{int} is the actual internal resistance of the element, was 0.62. This increase in the R_{int} value is attributed to the contact resistance between the Mg_2Si and the Ni electrode. To diminish the contact resistance, introducing a high-carrier-density layer of Mg_2Si between the electrode and the Mg_2Si may be effective; however this work is still underway. Additionally, optimization of the sintering process is needed to improve the MF value. Optimization of the shape, including the width, length, and height of the element, will also improve its output power density. In terms of the durability of the material, the Al-doped Mg_2Si used in this study is not stable at elevated temperatures. Although, it has already been confirmed that the durability at elevated temperatures of Sb-doped Mg_2Si is better than that of Al-doped Mg_2Si, the sintering process for the formation of electrodes on Sb-doped Mg_2Si has not been completed at present. Therefore, we used Al-doped Mg_2Si as a source material for the TE elements in this work. Developing the sintering process to form electrodes on Sb-doped Mg_2Si is a subject of our future work.

The results of the I–V characteristics and the output power measurements with a load resistance for the module with various temperature differences, ΔT, ranging from 100 K to 500 K are shown in Fig. 5, and the number of elements used for the TE module, the total resistances of the TE elements, and the internal resistance of the module at room temperature are summarized in Table II. The heater block was heated at 473 K to 873 K, whereas the cooling block was maintained at 373 K. The measured open-circuit voltage, V_{OC}, of the module was 303 mV at ΔT = 300 K, 446 mV at ΔT = 400 K, and 594 mV at ΔT = 500 K. The measured maximum output power ($P_{\max}$) with a load resistance was 193 mW (1288 mA, 150 mV) at ΔT = 300 K, 354 mW (1529 mA, 232 mV) at ΔT = 400 K, and 542 mW (1728 mA, 314 mV) at ΔT = 500 K. A power density of 135.5 mW/cm^2 calculated for elements with area of 20 mm × 20 mm was observed. The observed maximum output power of 542 mW is lower than the expected value of 1089 mW (121 mW × 9), which is simply estimated from the output power of a single element. This decrease in output power of the module may be mainly due to a increase in internal resistance of the module, because the maximum output power, $P_{\max}$, is defined as follows:

$$P_{\max} = \left(\frac{V_{\mathrm{OC}}}{2R_{\mathrm{in,M}}}\right)^2 R_{\mathrm{in,M}},$$

when $R_{\mathrm{load}} = R_{\mathrm{in,M}}$. R_{load} and $R_{\mathrm{in,M}}$ are the values of the load resistance and the internal resistance in the module. $R_{\mathrm{in,M}}$ is the sum of $R_{\mathrm{E,total}}$, $R_{\mathrm{t,total}}$, and $R_{\mathrm{c,total}}$. $R_{\mathrm{E,total}}$ is the total resistance of the elements, $R_{\mathrm{t,total}}$ is the total resistance of the Ni terminals, and $R_{\mathrm{c,total}}$ is the total contact resistance between the elements and the Ni terminals. As shown in the formula, the value of $R_{\mathrm{in,M}}$ affects the value of $P_{\max}$. As shown in Table II, since the measured $R_{\mathrm{in,M}}$ at room temperature and $R_{\mathrm{E,total}}$ were 75.4 mΩ and 52 mΩ, respectively, and the calculated resistance of the Ni terminals using the electrical resistivity of Ni, $R_{\mathrm{t,total}}$, was 11.7 mΩ, the $R_{\mathrm{c,total}}$ value of our module was estimated to be about 11.7 mΩ. Therefore, the internal resistance, except for the resistance of the elements, $R_{\mathrm{t,total}} + R_{\mathrm{c,total}}$ was 23.4 mΩ. This increase in internal resistance due to $R_{\mathrm{t,total}} + R_{\mathrm{c,total}}$ is one of the reasons for the decrease in output power of our module. With a uni-leg structure module, an increase in the electrical resistance due to the resistance of the parts joining the elements cannot be avoided. Therefore, for the module performance, it is important to reduce the contact resistance. There is another reason for the decrease in module perfor-

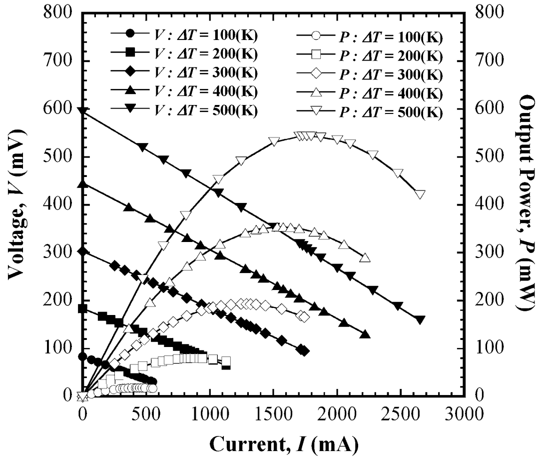

Fig. 5. The results of the I–V characteristics and the output power measurement with a load resistance for the module with various temperature differences, ΔT, ranging from 100 K to 500 K.

Table II. Number of Elements used for the TE Module, the Total Resistances of the TE Elements and Ni Terminals, and the Internal Resistance of Module

Number of Elements	Measured Internal Resistance of the Module at RT, $R_{\mathrm{in,M}}$ (mΩ)	Measured Total Resistance of Elements at RT, $R_{\mathrm{E,total}}$ (mΩ)	Calculated Total Resistance of the Terminals at RT, $R_{\mathrm{t,total}}$ (mΩ)	Calculated Contact Resistance of the Module, R_{c} (mΩ)
9	75.4	52	11.7	11.7

mance. The observed V_{OC} value of the module, 594 mV, is lower than the expected value of 828 mV (92 mV × 9), which was simply estimated from the V_{OC} value of a single element. The reduced V_{OC} value of the module may be mainly due to the thermal resistance of the electrically insulating Al_2O_3 plate and thermal conduction of the Ni terminals, because the thermal resistance of the Al_2O_3 plate is high and the Ni terminals connect the hot side of one element with the cold side of a neighboring element. Although the thermal insulation board was installed in the module in order to avoid thermal transportation, such as thermal conduction, thermal convection of air, and thermal radiation from the heat source to the cold side of the module via the gaps between each element, the effect of this is still unclear.

CONCLUSIONS

A uni-leg structure TE module comprising nine TE elements fabricated by a plasma-activated sintering method using commercial polycrystalline Mg_2Si was fabricated and evaluated. Evaluation of the output characteristics of the TE element and the module was performed at a temperature difference, ΔT, ranging from 100 K to 500 K. The observed open-circuit voltage and the maximum output power of the Mg_2Si TE element with Ni electrodes were 92 mV and 121 mW (2623 mA, 46 mV), respectively, at $\Delta T = 500$ K. The increase in internal resistance of the element due to the electrical contact resistance between the Ni electrodes and the Mg_2Si was confirmed. The measured open-circuit voltage and maximum output power of the module were 594 mV and 542 mW (1728 mA, 314 mV), respectively, at $\Delta T = 500$ K. Compared with the open-circuit voltage and the output power of a single element, those of the module were slightly lower. This decrease in the performance of the module may be caused by the contact resistance between the elements and the Ni terminals, thermal conduction of the Ni terminals, and the thermal resistance of the electrically insulating Al_2O_3 plate. Therefore, decreases in the contact resistance and the thermal loss in the module are necessary to improve its performance. Additionally, optimization of the shape, including the width, length, and height of the element, and an improvement in the occupancy rate of the elements in the module will be the subject of our future work.

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