Transactions of the Materials Research Society of Japan 32[3] 701-704 (2007)

Jointing technique and power generation characteristics of p-$NaCo_2O_4$/n-ZnO oxide thermoelectric modules

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A prototype of oxide thermoelectric module consisting of p-$NaCo_2O_4$/n-ZnO sintered materials was successfully fabricated for electrical power generation by applying a diffusion welding technique without filler metals. The power generation characteristics examined in the high temperature region revealed that the diffusion welding technique under a condition of 16 MPa at 1023 K in Ar was suitable to joint the sintered oxide materials with silver conducting strips. Twelve pairs of p- and n-oxides were connected in series with a planar arrangement in a square area of 30×30 mm^2. A maximum power output of 58 mW was obtained at a temperature condition of T_H/T_L = 839/377 K, and no deterioration in power output was observed even after twenty times of heat cycling.

Key words: Waste heat recovery, Thermoelectric materials, Oxide, Thermoelectric module, Power output

1. INTRODUCTION

Waste heat recovery is an important subject to save energy resources and to protect global environment. Thermoelectric power generation has been identified as a powerful candidate to provide an excellence solution for the waste heat recovery issues, because it directly converts heat into electrical energy irrespective of the size of the sources. A number of studies have been carried out to fabricate practical thermoelectric power generation modules using commercially available thermoelectric materials such as Bi-Te and Pb-Te alloys. However, these conventional materials are generally toxic, expensive, and unstable at high temperature in air, being fatally disadvantageous to be applied for practical mid-to-high temperature applications. Recently, oxide thermoelectric materials have started to be developed with an anticipation for overcoming these problems, and the thermoelectric performance of these materials has come to be comparable to those of the conventional thermoelectric materials. However, there have been few data on fabrication of thermoelectric modules using such attractive oxide materials.

Matsubara *et al.* fabricated an oxide thermoelectric device containing eight couples of Gd-doped p-type $Ca_3Co_4O_9$ and La doped n-type $CaMnO_3$ on a plate-type fin [1]. Their device showed an open circuit voltage (V_o) of 0.988 V and a maximum power output (P_{max}) of 63.5 mW at the temperature condition of T_H/T_L = 1046/656 K. Very recently, Funahashi *et al.* fabricated a portable oxide thermoelectric device consisting of 140 pairs of p-$Ca_{2.7}Bi_{0.3}Co_4O_9$ and n-$La_{0.9}Bi_{0.1}MnO_3$ bulks in a planar arrangement, and the V_o and P_{max} were reached as 4.5 V and 150 mW, respectively, at T_H/T_L = 1072/521 K [2]. However their jointing technique of p- and n-materials with the metal electrodes was limited only for brazing method using Ag-paste. Although the brazing method using filler metals is a popular technique to make metal junctions for high temperatures, optimization of filler metals is a time consuming task. In fact, Funahashi had to develop an original recipe of an Ag-paste containing oxide thermoelectric materials in order to reduce contact resistance at the p-n junctions [3]. On the other hand, Shin *et al.* tried to make a p-n junction between Li-doped p-NiO and n-$Ba_{0.2}Sr_{0.8}PbO_3$ materials by applying a simultaneous sintering technique without conducting strips [4]. However the technique is unsuitable to make practical thermoelectric modules with a planar arrangement.

In the past decade, we have developed sintered p-$NaCo_2O_4$ and n-ZnO materials as promising oxide thermoelectric materials. The maximum ZT values of the p-$NaCo_2O_4$ and n-ZnO reached 0.78 [5] and 0.3 [6], respectively. As a next stage of the development of the materials, we have planned on fabricating a prototype thermoelectric module using these materials. Fig. 1 gives a conceptual drawing of a π-shaped oxide thermoelectric module containing the p-$NaCo_2O_4$ and n-ZnO materials. As shown in Fig. 1, the module consists of twelve pairs of p-n couples with a planar arrangement in a square area of 30 x 30 mm^2. As is in the conventional π-shaped modules using such as Bi-Te and Pb-Te alloys, the oxide legs are connected via thin conducting strips (metal electrodes). For jointing the oxide materials with the conducting strips, we have tried to adopt a diffusion welding method, which is also a common technique to establish a firm connection between two materials for high temperature applications. It should be noted that the diffusion welding method needs no filler metals, being expected to shorten the project term for developing oxide thermoelectric modules. Our goal is to establish a filler-metal-free jointing technique for fabrication of oxide thermoelectric modules consisting of *p*-$NaCo_2O_4$ and *n*-ZnO legs for power generation applications utilizing waste heat in the high temperature region around 773 K (500 °C).

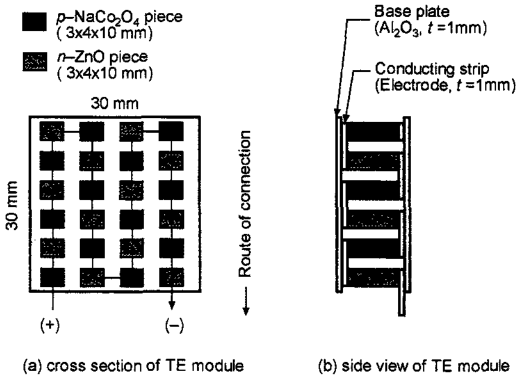

Fig. 1: Conceptual drawings of the prototype oxide thermoelectric module consisting of the *p*-$NaCo_2O_4$ and *n*-ZnO sintered oxide legs.

2. EXPERIMENTAL DETAILS

In this study, *p*-$NaCo_2O_4$ was synthesized by a conventional solid-state reaction from commercially purchased Na_2CO_3 and Co_3O_4 powders of the reagent grade. As reported in a previous paper [5], the powders were weighed at a ratio of Na:Co = 1.1:2.0, and mixed in a ball mill using nylon balls with ethanol for 24 h. The mixture was calcined as the first reaction at 1073 K for 12 h in air. In order to compensate the Na loss during the reaction, 10% excess of Na_2CO_3 powder was added to the reacted powder, and then calcined as the second reaction under the conditions same to those for the first reaction. The resulting powder was mixed again with 10 % excess of Na_2CO_3, and was shaped into a disk by cold isostatic pressing (CIP) at a pressure of 147 MPa, and then finally sintered at 1173 K for 12 h in air. The XRD patterns measured by using the test pieces showed that the sintered disks had enough purity to employ the resulted material as *p*-type thermoelectric pieces, whereas small amount of Co_3O_4 phase was observed.

Sintered bodies of *n*-ZnO were prepared by a direct sintering process using a commercial ZnO powder. In order to enhance the electrical conductivity, 2 mol% of γ-Al_2O_3 was added to the ZnO powder, which amount of γ-Al_2O_3 was systematically optimized in the previous research [6]. The mixed powder was pulverized by using a ball mill with nylon balls in ethanol for 20 h. The mixed powder was pressed into a disk by CIP at 147 MPa, and was sintered at 1673 K for 10 h in air.

In this study, we examined four candidate materials for the conducting strips (metal electrodes); nickel (Ni), cupper (Cu), platinum (Pt), and silver (Ag). Fig. 2 shows a schematic illustration of the diffusion welding apparatus. A series of diffusion welding tests was carried for the four candidates in order to select the best match to the oxide thermoelectric legs. As shown in Fig. 2, a Mo plate was placed at the bottom of the chamber as a metal base. A candidate metal strip (electrode) was placed on the Mo plate, and the sintered oxide leg was set on the electrode. A firm contact between the sintered oxide and the electrode was maintained by a vertical force of 50 N loaded from the top of the sintered oxide. Ar gas with a flow rate of 10 L/min was introduced to the chamber in order to prevent oxidation of the materials. The set of the sintered oxide and the electrode was heated by induction heating using high-frequency coils around the graphite shroud, and the temperature during the heating process was measured by a thermocouple attached at the top of the chamber base.

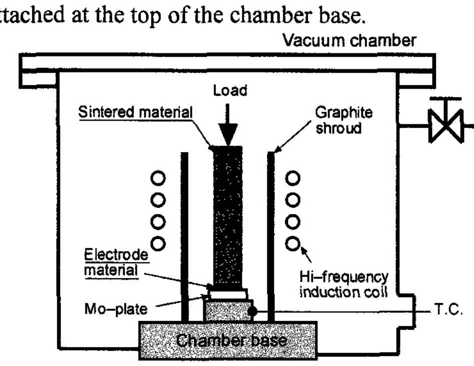

Fig. 2: A schematic illustration of the diffusion welding test for the conducting strips.

In order to evaluate the electrical performance of the oxide thermoelectric modules, we employed a thermoelectrical measurement system PEM-1 (ULVAC RIKO Co. Ltd) and an external circuit. Fig. 3 indicates a schematic diagram of the configuration of PEM-1 and the external circuit. As shown in Fig. 3, the module was sandwiched between Ni and Cu blocks via thin blocks for thermocouples (type K), and carbon sheets were inserted at each contact between the blocks to ensure the heat conduction along the vertical direction. In order to prevent horizontal heat leaks from the stack, small hollow beads were filled around the stack for heat insulation as shown in Fig. 3, and the chamber was evacuated to high vacuum by using a diffusion pump (DP). The upper side of the module was heated by an infra-red radiation heater via a receiving disk and the Ni block, and the lower side was cooled by the circulating water via the Cu block. The voltage and current generated by the module were measured using two KEITHLEY 2001 digital multimeters. A variable resistance was used as an external load resistance (R_L) in the circuit.

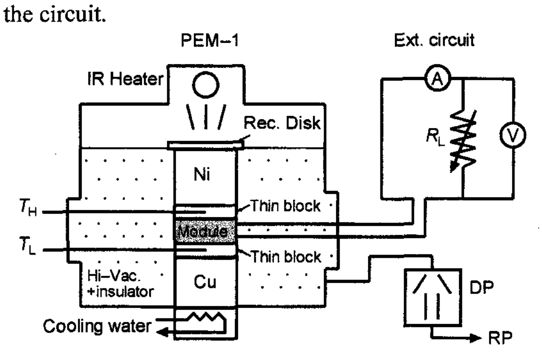

Fig. 3: A schematic diagram of PEM-1 (ULVAC RIKO Co. Ltd) and the external circuit for power generation measurement.

3. RESULTS AND DISCUSSION

(a) Diffusion welding test

A diffusion welding temperature is usually limited to be lower than a melting or a decomposition temperature of the materials involved, whereas higher welding temperature generally leads to higher mechanical strength. In this study, the welding temperature was decided as 1003 K, which is slightly lower than the calcined temperature of 1073 K for the p-$NaCo_2O_4$ materials. The time and load for the diffusion welding for the p-$NaCo_2O_4$ materials were selected as 3 min and 50 N, respectively. Table I summarizes the results of the diffusion welding test of the electrode candidates to sintered p-$NaCo_2O_4$. It was found that silver is the best material to meet requirements for the mechanical strength, electrical conductivity, and cost performance.

Table I: Results of diffusion welding test of the electrode candidates to sintered p-$NaCo_2O_4$.

Electrode candidate	Mechanical [-]	Resistace [Ω]	Cost [-]
Ni	X	-	-
Cu	O	750	-
Pt	O	0.071	X
Ag	O	0.070	O

Temperature: 1003 K, Time: 3 min, Load: 50 N,
Atmosphere: Ar (10 L/min)

(b) Preparation of uni-couple

We prepared a thermoelectric uni-couple employing the conditions thus optimized. Fig. 4 gives a photograph of the uni-couple consisting of the p-$NaCo_2O_4$ and n-ZnO sintered materials. As shown in Fig. 4, both the sintered oxides were firmly jointed to the Mo plate via Ag thin electrodes (t = 50 μm), indicating that the diffusion welding technique under the present conditions is suitable not only for the p-$NaCo_2O_4$ but also for the n-ZnO materials. The overall resistance of the uni-couple was 147 mΩ.

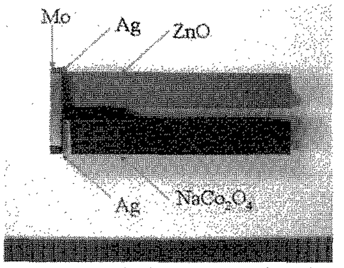

Fig. 4: Photograph of the thermoelectric uni-couple consisting of the p-$NaCo_2O_4$ and n-ZnO sintered materials connecting via a Mo plate (scale in mm).

(c) Fabrication of proto-type oxide thermoelectric module

Taking the above results into consideration, small sintered pieces of p-$NaCo_2O_4$ and n-ZnO aligned in the planar arrangement presented in Fig. 1 were connected to silver plate electrodes (t = 1 mm) by using the diffusion welding technique under a pressure of 16 MPa at 1023 K in Ar. Fig. 5 shows a photograph of the resulting prototype oxide thermoelectric module fabricated by the diffusion welding. Both sintered oxides of p-$NaCo_2O_4$ and n-ZnO were firmly welded to the silver conducting strips, and the twelve p-n couples were connected in series in a square area of 30 x 30 mm^2 as shown in Fig. 5. The height of the module thus obtained was approximately 14 mm, indicating that shrinkage of the components was minimal against the pressure of 16 MPa at the diffusion welding. Two silver plate electrodes at the both ends of the series connection come out from the module to serve as the plus (left) and minus (right) output terminals.

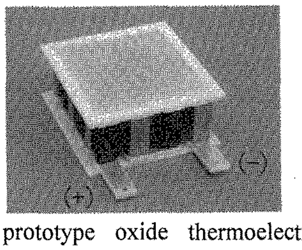

Fig. 5: A prototype oxide thermoelectric module fabricated by diffusion welding under 16 MPa at 1023 K in Ar.

(d) Power generation characteristics

In this study, electrical power generation characteristics of the prototype oxide thermoelectric module were examined at above 773 K at the hot side of the module. The external resistance (R_L) of the circuit presented in Fig. 3 was varied from $R_L = \infty$ (circuit open) to zero (circuit close) under the same temperature conditions. Fig. 6 shows typical I-V and I-P characteristics of the prototype oxide thermoelectric module, where T_H and T_L are the temperatures at the hot and cold sides of the base plates, respectively.

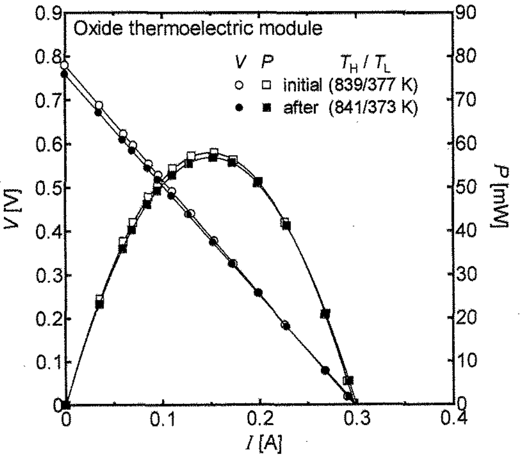

Fig. 6: Voltage (V) and power output (P) as a function of current (I) for the prototype oxide thermoelectric module consisting of 12 couples of p-$NaCo_2O_4$ and n-ZnO sintered oxides. The fitted lines for the I-V and I-P curves were calculated by the least-squares method using the relations of $V \propto I$ and $P \propto I^2$, respectively. Open and filled symbols indicate initial and final values for the heat-cycle test between 473 and 773 K for 20 times.

As shown by the open symbols in Fig. 6, the initial value of the open circuit voltage (V_o) of the module was 0.78 V, and the voltage decreased linearly with increasing current; the voltage reached zero at I = 0.29 A.

The internal resistance of the module was calculated to be 2.62 Ω from the slope of the fitted *I-V* curve. The power output increased with increasing current, taking a maximum value of 58 mW at I = 0.15 A, and then decreased again and reached zero at I = 0.29 A. This behavior fits well with the relation of $P \propto I^2$ as shown in the fitted curve in the Figure. After the initial measurement, we have further carried out a durability test by applying twenty times of heat cycles between 473 K and 773 K with an interval of 1 h. The *I-V* and *I-P* curves after heat cycles were also measured at the same temperature conditions. As shown in Fig. 6, the initial and final vales are virtually the same, indicating that the prototype oxide has a sufficient durability. The present jointing technique, diffusion welding without filler metals, is thereby concluded to be suitable to fabricate oxide thermoelectric modules, at least for those with the sintered *p*-$NaCo_2O_4$ and *n*-ZnO materials.

Table II: Comparison of materials and performance of oxide thermoelectric modules.

Author	Materials	*p-n* couples *N*	Arrangement	Conducting strip	Jointing technique	T_H [K]	T_L [K]	ΔT [K]	V_o [V]	P_{max} [mW]	$P_{max}/\Delta T$ [mW/K]
Present work	*p*- $NaCo_2O_4$ *n*- ZnO	12	Planer	Ag-plate	Diffusion welding	839	377	462	0.78	58.1	0.126
Matsubara [1]	*p*- $(Ca, Gd)_3Co_4O_9$ *n*- $CaMnO_3$	8	In-line	Pt-wire	Pt-paste	1046	656	390	0.988	63.5	0.163
Funahashi [2]	*p*- $Ca_{2.7}Bi_{0.3}Co_4O_9$ *n*- $La_{0.9}Bi_{0.1}NiO_3$	140	Planer	Ag-electrode	Ag-paste (original)	1072	521	551	4.5	150	0.272
Shin [4]	*p*- Li-doped NiO *n*- $BaPbO_3$	4	In-line	Non	Sintering	1164	625	539	0.39	34.4	0.064

Finally, we have compared various oxide thermoelectric modules studied by the present and other researchers. Table II summarizes specifications, running conditions, and performance of various oxide thermoelectric modules. Matsubara *et al.* fabricated the oxide thermoelectric device containing eight couples of *p*-$Ca_{2.75}Gd_{0.25}Co_4O_9$ and *n*-$CaMnO_3$ on the plate-type fin, and the power output (P_{max}) of 63.5 mW and the open circuit voltage (V_o) of 0.988 V were obtained under the temperature condition of T_H/T_L = 1046/656 K [1]. Shin *et al.* prepared the oxide thermoelectric module consisting of four couples of *p*-type Li-doped NiO and *n*-type $Ba_{0.2}Sr_{0.8}PbO_3$, and the module showed a P_{max} of 34.4 mW and a V_o of 0.39 V at T_H/T_L = 1164/625 K [4]. However, the configuration of *p-n* couples in these modules was limited as an in-line arrangement, implying that the modules would be difficult to apply for practical use. Funahashi *et al.* built a high-voltage type power generation system consisting of 140 pairs of *p*-$Ca_{2.7}Bi_{0.3}Co_4O_9$ and *n*-$La_{0.9}Bi_{0.1}MnO_3$ bulks in planar arrangement, which is the same configuration as that in the present study, and reported P_{max} of 150 mW and a V_o of 4.5 V at T_H/T_L = 1072/521 K [2].

As shown in Table II, the present prototype module showed a maximum power output (P_{max}) competitive to other oxide modules except the 140-pairs one, whereas the T_H of the present module was much lower than those of other three modules. It is notable that the implement density of the present module is only 32 %, because the present module was predominantly designed as a prototype to develop the jointing technique between the oxide thermoelectric materials and the electrode materials. Whereas the implement density of our module can therefore increase further, the Funahashi's module has little chance because of its already high implement density [2]. As a next step, we are planning on improving the power generation performance of the oxide modules by increasing the implement density up to 85%. As a result, the $P_{max}/\Delta T$ value is expected to reach 0.334 mW/K, which is higher than that of the Funahashi's module. In addition, we are also considering a chemical analysis of the diffusion layers between the thermoelectric oxides and the silver plate electrodes in the present module to reduce the contact resistance in the layers.

4. CONCLUSIONS

We have successfully fabricated a prototype oxide thermoelectric module consisting of twelve couples of sintered *p*-$NaCo_2O_4$ and *n*-ZnO materials using diffusion welding technique. The welding conditions of 16 MPa at 1023 K in an Ar atmosphere were suitable to joint these materials to silver conducting strips (electrodes) in order to fabricate a series connection through alternating *p* and *n* oxide legs in a planar arrangement. The open circuit voltage and the maximum power output were obtained as 0.78 V and 58 mW at the temperature condition of T_H/T_L = 839/377 K, and no deterioration in performance was observed even after the heat-cycling examination of twenty times. The present results will be helpful for development of oxide thermoelectric modules as practical power generation systems for waste heat recovering around 773 K.

5. REFERENCES

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(Received January 20, 2007;Accepted May 10, 2007)